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CONTENTS.

A. F. Holleman and G. L. Voerman: "α- and β-thiophenic acid", p. 514.

J. D. van der Waals: "A remark on the theory of the ψ-surface for binary mixtures", p. 524.

W. A. Wijthoff: "The rule of Neper in the four-dimensional space". (Communicated by Prof. P. H. Schoute), p. 529.

P. H. Schoute: "The locus of the cusps of a threefold infinite linear system of plane cubics with six basepoints", p. 534.

W. J. H. Moll: "An investigation of some ultra-red metallic spectra". (Communicated by Prof. W. H. Julius), p. 544.

F. Schuh: "On the locus of the pairs of common points and the envelope of the common chords of the curves of three pencils", (2nd Communication. Application to pencils of conics). (Communicated by Prof. P. H. Schoute), p. 548.

F. Schuh: "The locus of the pairs of common points of four pencils of surfaces". (Communicated by Prof. P. H. Schoute), p. 555.

C. H. Wind, A. F. H. Dalhuisen and W. E. Ringer: "Current-measurements at various depths in the North-Sea", (1st Communication), p. 566. (With one plate).

F. Schuh: "The locus of the pairs of common points of $n+1$ pencils of $(n-1)$ dimensional varieties in a space of n dimensions". (Communicated by Prof. P. H. Schoute), p. 573.

H. G. van de Sande Bakhuyzen: "On the astronomical refractions corresponding to a distribution of the temperature in the atmosphere derived from balloon ascents", p. 578.

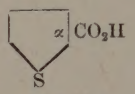
H. Zwaardemaker: "An investigation on the quantitative relation between vagus stimulation and cardiac action, an account of an experimental investigation of Mr. P. Wolterson", p. 590.

Erratum, p. 598.

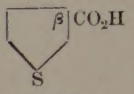
Chemistry. — "*α- and β-thiophenic acid.*" By Prof. A. F. HOLLEMAN and Dr. G. L. VOERMAN.

(Communicated in the meeting of December 29, 1907).

A very remarkable research on these acids was published in 1886 by V. MEYER, who discovered the same. In the main it amounts to this, that in addition to the theoretically possible monocarboxylic acids of thiophen



Mp. 126°.2



Mp. 138°.4

a third isomer was obtained, called *α*-thiophenic acid m.p. 117.5—118°, which, however, in its derivatives such as the amide, the phenylurea derivative of the amide, the amidoxime and the thienone $(C_4H_3S)_2CO$, so completely resembled the corresponding derivatives of the *α*-acid that they would have been declared identical, were it not that from the *α*-derivates the *α*-acid m.p. 118° was regenerated, whilst the *α*-derivates yielded the *α*-acid m.p. 126°. V. MEYER expresses himself as follows: "Die Vergleichung der *α*- und *α*-Säure ergab immer von "Neuem das merkwürdige Resultat, dass die beiden Säuren wirklich "in ihren Eigenschaften durchaus verschieden sind, und dass die Ver- "schiedenheiten sich als constante, durch keinerlei Reinigung oder "Umwandlungen zu entfernende Eigenschaften erwiesen; dass aber "alle Derivate der beiden Säuren in ihren physikalischen Eigenschaften "absolut zusammenfallen und für identisch (im gewöhnlichen Sinne) "erklärt werden müssten, wenn sie nicht die Eigenschaft besässen, "dass jedes aus der *α*-Säure dargestellte Derivat bei der Rückführung "auch wieder *α*-Säure, jedes *α*-Derivat dagegen *α*-Säure lieferte."

As the *α*-acid had also been obtained by oxidation of tar-thiotolene which is a mixture of *α*- and *β*-thiotolene [2—3 methylthiophen], V. MEYER suspected that this *α*-acid might be after all a mixture of *α*- and *β*-acid, and he really succeeded, by oxidation of a mixture of the two thiotolenes in definite proportion, or by slow crystallisation of a mixture of *α*- and *β*-acid from cold water, in obtaining an acid which agreed in every respect with the *α*-acid. This was no doubt an important step forward, but the behaviour of such a mixture and also of the derivatives obtained therefrom still remained a very remarkable one.

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[1]) A. **236**, 200; also V. MEYER, die Thiophengruppe p. 188—207.

Notwithstanding all this, nobody, since this elaborate research of V. MEYER, has been engaged during the last 20 years in the study of these acids, although it might have been expected from the development of the phase-rule that the latter might possibly give us a closer insight into the phenomena described above.

The probable cause of all this is that these acids are not readily accessible, and that those engaged in researches connected with the phase-rule have not ventured to prepare the same. When Dr. VOERMAN, at my request, undertook the closer study of these acids we had, first of all, to find a better process for the preparation of these substances.

In the case of the α-acid we have indeed succeeded in a very satisfactory manner. We have also worked out another and improved method for the preparation of the β-acid; but it is still unsatisfactory owing to the small yield. Therefore, we have been obliged to restrict ourselves, provisionally, to the study of the acids themselves; the derivatives will be taken in hand when more material has been obtained.

Preparation of α-thiophenic acid. By V. MEYER and his pupils, this acid was best obtained by oxidation of propiothienon $C_4H_3S.COC_2H_5$, because the oxidation of the much more readily accessible acetothienon $C_4H_3S.COCH_3$ yielded a mixture of α-thiophenic acid and thienylglyoxylic acid, which it was rather troublesome to separate. We have succeeded in converting acetothienon almost quantitatively into α-thiophenic acid, being guided by the following considerations. If we oxidise a methyl ketone, experience has taught that the methyl group very readily changes to carboxyl thus forming a glyoxylic acid: $R.CO.CH_3 \rightarrow R.CO.CO_2H$. If, however, we attempt to go further and obtain the corresponding carboxylic acid: $R.CO.CO_2H \rightarrow R.CO_2H$ a difficulty is experienced and the oxidising mixture then also attacks the group R so that the yield of the carboxylic acid becomes generally unsatisfactory. Now some time ago, I found a method for converting acids $R.CO.CO_2H$ quantitatively into $R.CO_2H$; this is rendered possible by the application of hydrogen peroxide which causes a ready resolution according to the scheme:

$$\begin{matrix} R.CO.CO_2H \\ HO\ \ OH \end{matrix} = R.COOH + CO_2 + H_2O$$

This method has led to the desired result in this case. The oxidation of acetothienon is, therefore, done in two stages, first the formation of thienylglyoxylic acid which is subsequently oxidised to -thiophenic acid. The practical application of these processes was as follows:

Acetothienon was prepared from thiophen according to the method of FRIEDEL and CRAFTS, and a very good yield was obtained. The thiophen was prepared by ourselves by distillation of sodium succinate with P_2S_3. 11.5 grams of ketone and 12 grams of sodium hydroxide were introduced into a litre of water, and to this was added slowly, at the ordinary temperature, a solution of 42 grams of potassium permanganate dissolved in a litre of water. After each addition the pink colour was allowed to change to green before addition of a fresh portion.

After all the permanganate had been added the liquid was allowed to remain overnight; the solution was heated gently on the waterbath until the green colour had disappeared, then filtered off from the manganese dioxide, and concentrated to 250 cc. Without isolation of the thienylglyoxylic acid, beforehand the liquid, after being *nearly* neutralised with hydrochloric acid, is mixed with 9 grams of 30 % hydrogen peroxide previously diluted with its own volume of water. The whole is set aside for a few hours, and afterwards heated for a few moments on a waterbath. On acidification the liquid the greater part of the α-thiophenic acid formed is precipitated in a pure condition; a further small quantity may be recovered from the mother-liquor by extraction with ether. By recrystallisation from water and distillation in vacuo, the acid may be obtained pure and quite free from thienylglyoxylic acid. The yield amounts to about 9 grams.

The solution of α-thiophenic acid saturated at 24°.9 contains 0.75 %.

Preparation of β-thiophenic acid. V. MEYER has effected this by oxidising with potassium permanganate in very dilute, cold solution. The yield of β-acid was however very poor, in fact only about 5—8 % of the thiotolene employed. After trying various modifications of this direct oxidation process without arriving at a better result we decided to follow an indirect way by first chlorinating the side chain, then preparing the aldehyde from the thienalchloride and finally oxidising the former to the acid:

$$C_4H_3S \cdot CH_3 \rightarrow C_4H_3S \cdot CHCl_2 \rightarrow C_4H_3S \cdot CHO \rightarrow C_4H_3S \cdot COOH.$$

Bearing in mind VAN DER LAAN'S research [1]) on the bromination of toluene where it was shown that in presence of PCl_5 the substitution in the side chain is accelerated, this substance was added in the chlorination of β-thiotolene. The above mentioned processes all proceeded very smoothly, but unfortunately an acid rich in chlorine was finally obtained as, apparently, the chlorination had also extended to the nucleus. This certainly could be freed from chlorine by treatment with sodium-amalgam but a large proportion of the β-thiophenic acid was lost thereby so that the yield did, finally, not exceed 10 % of the thiotolene employed.

We add a few particulars as to the *modus operandi* followed.

β-thiotolene was prepared by ourselves by distilling sodium pyrotartrate with phosphorus trisulphide. The chlorination took place in direct sunlight in the presence of 10 % of PCl_5. The reaction product is boiled in a reflux apparatus with water and calcium carbonate. The aldehyde is distilled in steam and purified over the

[1]) These Proc. Oct. 1905).

bisulphite compound. From 10 grams of thiotolene about 5 grams of the aldehyde are obtained. Of this, 3 grams are oxidised with 500 cc. of water containing 3.2 grams of potassium permanganate and 1.3 gram of 80 % potassium hydroxide; after standing over night the liquid is filtered from the manganese dioxide, concentrated and acidified when about 3 grams of thiophenic acid are precipitated. The dechlorination of this product with sodium amalgam in dilute aqueous solution takes 15—20 days during which a large portion of the acid gets lost.

As regards the solubility of β-thiophenic acid at 25° it was found that the saturated solution contains 0.43 % of acid.

Melting point line of mixtures of the two acids. According to the present views of the phase rule it was natural to suppose that the impossibility of separating these acids by crystallisation is due to the fact that they yield mixed crystals. In fact by determining the melting point line, Dr. VOERMAN has succeeded in demonstrating with certainty that they give an interrupted mixing series. The initial solidifying points may be observed very sharply but the final solidifying points can only be determined within 0°.5.

A list of the initial and final solidifying points is appended; and in the annexed curve these figures are represented graphically.

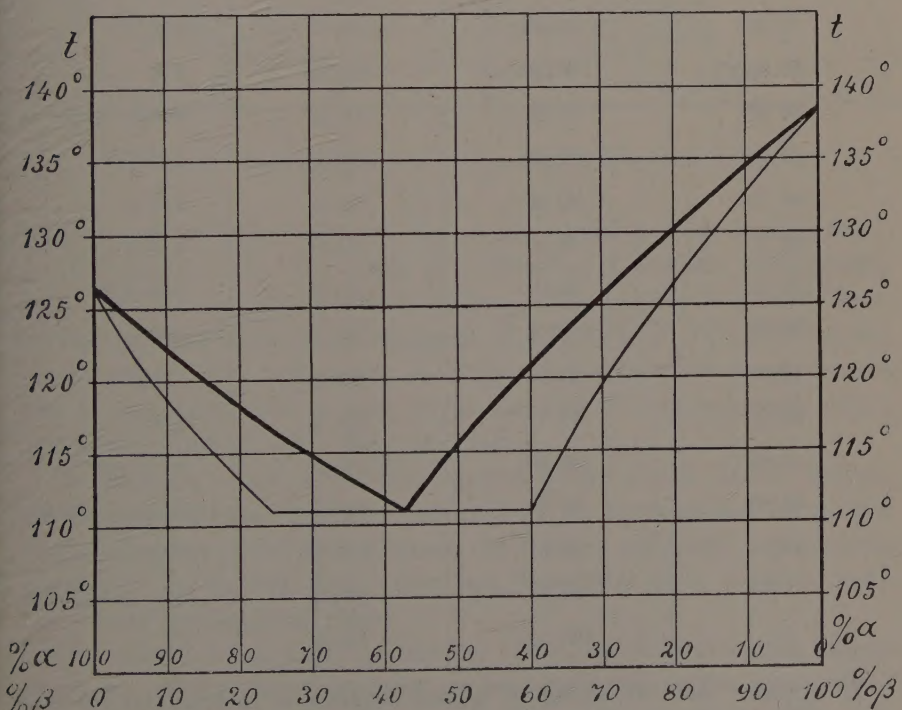

Fig. 1.

SOLIDIFYING POINTS OF α AND β-THIOPHENIC ACID AND THEIR MIXTURES.

% α	% β	1st solidifying point	2nd solidifying point
100	0	126°.2	
99.01	0.99	125.4	123°.9—124°.4
98.25	1.75	125.1	
96.56	3.44	124.6	123.1—123.6
94.3	5.7	124.1	121.0
93.60	6.40	123.4	
90.60	9.40	122.2	
88.20	11.80	121.3	± 118
85.82	14.28	120.3	± 116.6
85.0	15.0	120.1	
79.45	20.55	117.7	113.5—114
77.45	22.55	117.2	112 —112.6
75.3	24.7	116.3	110.8—111.2
74.60	25.40	116.0	± 110.6
69.45	30.55	114.3	110 —111
66.20	33.80	113.3	110.5—110.8
63.35	36.65	112.5	110.8
59.70	40.30	111.5	110.5
58.0	42.0	111.0	110.7
55.0	45.0	112.6	110.8
50.85	49.15	115.0	110.7
42.50	57.50	119.6	id.
38.9	61.1	121.2	111.2
33.60	66.40	124.0	116.5—117.5
23.80	76.20	128.2	123—124 (±123.5)
14.0	86.0	132.6	129.5—129.8
5.4	94.6	136.3	134 —134.3
0	100	138.4	

It appears that the series of mixed crystals is interrupted on one side at 25% β-acid, and on the other side at 61%; and that there is a eutectic point at 42.5% β-acid at a temperature of 111°.

The crystallographical investigation of these acids and their mixtures kindly carried out by Dr. JAEGER leads to exactly the same result. Dr. JAEGER reports as follows:

Of the two isomeric compounds *β-Thiophenic acid* crystallises the most readily in sharply defined, small crystalline plates.

Whether obtained by crystallisation from solvents or by fusion and subsequent cooling, the compound exhibits the microscopical appearance of the subjoined figure. The crystals are monoclino-pris-

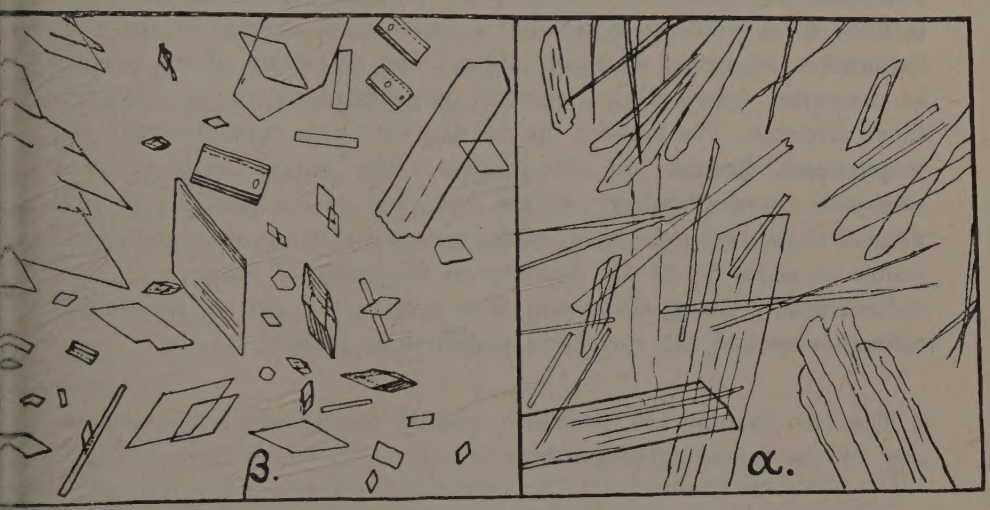

Fig. 2. Microscopcial aspect of α- and β-Thiophenic acid.

matic, and combinations of the form: {001}, very predominant, {110} and {100}; the angle of inclination β deviates considerably from 90°, so that the smaller individuals often exhibit rhomboidal form owing to simultaneous development of {110} and {001}. Often the plates are so thin that only a single parallelogrammatic circumference can be observed with a very slight stunting of the sharp angle which was determined at 42°—43°, by {100}.

In addition, small rectangular plates occur which, as the investigation shows, are formed with {100} as predominant form, and therefore show prolongation along the *b*-axis. Although representing apparently a second form they are, however, quite identical with the parallelogrammatic phase.

The optical axial plane is parallel {010} and falls along the longest diagonal of the parallelograms or perpendicular to the longitudinal direction of the needle-shaped individuals. In convergent light one hyperbole with rings is visible at the border of the field of vision.

Very feeble inclined dispersion with $\varrho > v$; double refraction negative. The longitudinal axis of the parallelograms and the shortest dimension (breadth) of the more needle-shaped individuals are the directions of a smaller optical elasticity.

α-Thiophenic acid crystallises from solvents or from the fused mass in long more or less broad needle-shaped individuals, which usually exhibit only a rudimentary limitation and cannot therefore be properly determined morphologically. Although the optical properties seem to point to a monoclinic symmetry one might also feel inclined to conclude to a triclinic symmetry on account of the form limitations occurring here and there. The extinction of the needles is, however apparently orientated perpendicularly to their longitudinal direction. The smaller optical elasticity axis coincides with the longitudinal direction of the needles. The optical axial plane is orientated perpendicularly to the longitude of the needles; in convergent light a single very characteristically coloured hyperbole is visible at about $^2/_3$ of the diameter of the fields of vision.

Enormously strong dispersion with $\varrho < v$; the sign of the double refraction around the correlated bissectrix is positive.

The two isomers are, therefore, readily distinguished microscopically by the following properties:

β-Thiophenic acid	*α-Thiophenic acid*
Parallellogrammic limitation, or short rods of rectangular form.	Long, very slender needles, mostly with rudimentary limitation.
Very high interference colours.	Grey, or unconspicuous colours.
One optical axis with elliptical rings, very weak dispersion $\varrho < v$.	One coloured hyperbole; very strong dispersion: $\varrho < v$.
Negative double refraction.	Positive double refraction.
Monoclinic symmetry; angle of the parallelograms 42°—43°.	Triclinic or monoclinic symmetry.
Optical axial plane for the parallelograms // to the longest diagonal for the needles perpendicular to the longitudinal direction.	The optical axial plane is perpendicular to the longitudinal direction of the needles. The latter coincides with the shortest elasticity-axis of the crystals.
The largest elasticity-axis is parallel to the longitudinal direction of the needles or to the shortest diagonal of the parallelograms.	

On account of the evaporation of the two substances when melting, one is obliged always to use a covering glass under the crystallisation-microscope.

On mixing the two isomers I have noticed the following on melting and subsequently cooling the mixtures.

a. Mixture containing 61,6 % of β-acid yields exclusively *mixed crystals* of the β-form; formation of *minute traces* of α-crystals is not improbable.

b. Mixture containing 42 % of β-acid yields chiefly *mixed crystals* of the α-form; at the edges of the fused mass, however, are found also *very small*, slightly coloured parallelograms of the β-form. Negative mixed crystals in the α-form (see *d*) were not noticed; only positive ones with $\varrho < v$.

c. Mixture containing 35,5% of β-acid behaves on solidification like *b*.

d. Mixture containing 22,5 % of β-acid, only yields mixed crystals of the α-form both positive and negative doubly-refracting but with $\varrho < v$ like the α-acid itself.

e. Mixture containing 86 % of α-acid only gives mixed crystals of the α-type with strong dispersion $\varrho < v$ and a positive double refraction.

Dr. JAEGER comes to the following conclusion:

"There exists here an isodimorphous mixing series with hiatus. This extends from a β-acid concentration $> 22{,}5\%$ to mixtures containing 61—62 % of the β-compound. The mixed crystals of the α-type become on addition of the negative β-compound less strongly positive optically and in the immediate vicinity of the hiatus even negative; they, however still retain the strong dispersion with $\varrho < v$, which is so characteristic for the pure α-compound.

On the other hand, the mixed crystals of the β-type have at all concentrations of 62—100 % a negative double refraction and a very feeble inclined dispersion."

V. MEYER states in his treatise that in the oxidation of mixtures of the two thiotolenes, he has obtained various other mixtures of α- and β-thiophenic acid, and that these showed no sign of separation into their components when subjected to fractional crystallisation.

Dr. VOERMAN, however, cannot confirm this observation. When he recrystallised a mixture of 85.3% α-acid and 14.7% of β-acid (solidifying point 120°.3) from hot water, the solidifying point increased to 121 .6 which corresponds with a mixture of 89% α- and 11% of β-acid. As, however, V. MEYER does not state the temperature at

which he carried out his fractional crystallisations, it is possible that this was not the same as in VOERMAN's experiment and this might account for the difference.

Dr. VOERMAN has finally been engaged in the determination of the conductivity power of the two acids and their mixtures in the hope of obtaining indications of a combination of the two acids when in solution. The observations are as follows:

CONDUCTIVITY POWER OF α-THIOPHENIC ACID AT 25°.

v	μ	α	100 k	
25	32.44	0.085	0.0314	
50	45.37	0.118	0.0319	
100	62.49	0.163	0.0319	
200	85.06	0.222	0.0318	$\mu_\infty = 382.7$
400	113.87	0.298	0.0315	
800	149.41	0.390	0.0312	
[1600	189.34	0.495	0.0303]	
			Average 0.0316	

In this table, v represents the volume in which 1 mol. is dissolved, μ the molecular conductivity power, α the degree of dissociation, 100 k the dissociation constant according to OSTWALD $\times$ 100.

The conductivity power has been determined, previously, by OSTWALD (Ph. Ch. **3**, 384) who found for 100 k 0,0302, and by BADER, (Ph. Ch. **6**, 313) who found for 100 k 0,0329.

CONDUCTIVITY POWER OF β-THIOPHENIC ACID AT 25°.

v		α	100 k	
50	23.20	0.061	0.00783	
100	32.32	0.084	0.00779	
200	44.90	0.117	0.007795	$\mu_\infty = 382.7$
400	62.06	0.162	0.00784	
800	84.66	0.221	0.00785	
[1600	114.17	0.298	0.00793]	
			Average 0.00783	

CONDUCTIVITY POWER OF MIXTURES OF $\alpha + \beta$-THIOPHENIC ACID AT 25°.

11% } thiophenic acid
89% α }

v	μ	α	100 k
50	43.26	0.113	0.0288
100	59.49	0.155	0.0286
200	80.94	0.211	0.0284
400	108.05	0.282	0.0278
800	141.29	0.369	0.0270
1600	180.75	0.572	0.0264

33.33% β } thiophenic acid
66.66%

v	μ	α	100 k
33.333	31.79	0.083	0.0226
66.666	44.28	0.116	0.0227
133.333	60.86	0.159	0.0226
266.666	82.33	0.215	0.0221
533.333	109.83	0.287	0.0217
1066.666	143.38	0.375	0.0210

50% β } thiophenic acid
50% α }

v	μ	α	100 k
50	35.12	0.092	0.0185
100	48.52	0.127	0.0184
200	66.01	0.172	0.0180
400	88.58	0.231	0.0174
800	117.15	0.306	0.0170
1600	151.7	0.396	0.0163

70.4% β } thiophenic acid
29.6% α }

v	μ	α	100 k
100	43.04	0.112	0.0143
200	58.63	0.153	0.0139
400	79.06	0.207	0.0135
800	105.02	0.274	0.0130
1600	138.20	0.361	0.0128

The conductivity of the pure β-acid has been determined previously by Lovèn (Ph. Ch. **19**, 458) who found :

$$100\,k = 0{,}0078.$$

which agrees well with the value found by myself.

The influence of the position of the sulphur atom in regard to the carboxyl group is very marked.

From these observations it appears that the acids in aequeous solutions exert but very little influence on their mutual conductivity power, as the conductivity power of the mixtures agrees fairly well with the calculated result. A condensation of their molecules in such a solution cannot therefore be supposed to take place.

Physics. — "*A remark on the theory of the ψ-surface for binary mixtures.*" By Prof. J. D. van der Waals.

(Communicated in the meeting of December 29, 1906).

Kamerlingh Onnes' startling experiment, in which a gas was obtained that sinks in a liquid, has drawn the attention more closely to the direction of the tangent in the plaitpoint of a binary mixture. Leaving the further particulars required for the realisation of such a mixture to the investigations of Kamerlingh Onnes and his collaborators, I will make a remark of general significance, in close connection with this experiment.

In my Théorie moléculaire and more fully in Cont. II I have examined the condition, on which the tangent in the plaitpoint runs parallel to the v-axis, or in other words $\left(\frac{dv}{dx}\right) = \infty$. The problems related to this may be reduced to 3. All three refer to the intersection of the two curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$.

As first problem I should like to regard the principal one, namely that where $\frac{\partial^2\psi}{\partial v^2} = 0$ and $\frac{\partial^2\psi}{\partial x\,\partial v} = 0$. The point considered lies, therefore, on the spinodal curve, and at the same time the curve $\frac{\partial^2\psi}{\partial v^2} = 0$ has for constant value of x two equal values for v and so also $\frac{\partial^3\psi}{\partial v^3} = 0$. Then the point considered is the critical point of the mixture taken as homogeneous. The value of T is that of T_k for such a mixture and the value of x is then found, when the approximate equation of state with b constant is applied, from :

$$\frac{\frac{1}{a}\frac{da}{dx}}{\frac{1}{b}\frac{db}{dx}} = \frac{2}{3},$$

which value $^2/_3$ becomes $= {}^6/_7$, when the independence of b of the volume is relinquished.

In this case the line $\frac{\partial^2\psi}{\partial x\,\partial v}$ cuts the line $\frac{\partial^2\psi}{\partial v^2} = 0$ still in two points. One point is that above mentioned, the second lies at smaller x and larger x. So nearer the component with the smallest value of b.

With increase of temperature the two points of intersection draw nearer to each other, and as second problem we may put: to examine the circumstances under which the two points of intersection of these curves coincide. The three equations from which this circumstance is determined, are then: $\frac{\partial^2\psi}{\partial v^2} = 0$, $\frac{\partial^2\psi}{\partial x\,\partial v} = 0$ and a third which expresses that these curves touch, viz.:

$$\left(\frac{\partial^3\psi}{\partial v^2\,\partial x}\right)^2 = \frac{\partial^3\psi}{\partial x^2\,\partial v}\,\frac{\partial^3\psi}{\partial v^3}$$

or

$$\left(\frac{\partial^2 p}{\partial x\,\partial v}\right)^2 = \frac{\partial^2 p}{\partial x^2}\,\frac{\partial^2 p}{\partial v^2}$$

Above the temperature at which these circumstances are fulfilled, $\frac{\partial^2\psi}{\partial v^2} = 0$ and $\frac{\partial^2\psi}{\partial x\partial v} = 0$ do not intersect any longer, and the complication in the course of the isobars, viz. that there is one that intersects itself, has disappeared.

The third problem is more or less isolated, but yet I should like to treat it in this connection: viz. that for which the line $\frac{\partial^2\psi}{\partial v^2} = 0$ has a double point, and so at the same time $\frac{\partial^3\psi}{\partial v^3} = 0$ and $\frac{\partial^3\psi}{\partial x\partial v^2} = 0$. If there is a minimum T_k for mixtures taken us homogeneous, such a point is really a double point. If there should be a maximum T_k, it is an isolated point. We find then again $v = v_k$, $T = T_k$ and the value of x is that for which T_k has a minimum or maximum value. Let us call the three values of x obtained for those three problems x_1, x_2 and x_3, then:

$$x_2 < x_1 < x_3$$
$$T_2 > T_1 > T_3.$$

Now there are three more problems, and to this I will call attention in this note, which may be considered as the analogues to the three above-mentioned ones.

If in the above problems we substitute the quantity x for v and vice versa, so that $\frac{\partial^2\psi}{\partial v^2}$ changes into $\frac{\partial^2\psi}{\partial x^2}$, and $\frac{\partial^2\psi}{\partial x \partial v}$ remains unchanged then the intersection of the curves $\frac{\partial^2\psi}{\partial x^2} = 0$ and $\frac{\partial^2\psi}{\partial x \partial v} = 0$ will give rise to three problems, which are of as much importance for the theory of the binary mixtures as the three above-mentioned problems, which relate to the intersection of $\frac{\partial^2\psi}{\partial v^2} = 0$ and $\frac{\partial^2\psi}{\partial x \partial v} = 0$.

In the first place the points at which the two curves $\frac{\partial^2\psi}{\partial x^2} = 0$ and $\frac{\partial^2\psi}{\partial x \partial v} = 0$ intersect will belong to the spinodal curve, as appears from $\frac{\partial^2\psi}{\partial x^2}\frac{\partial^2\psi}{\partial v^2} = \left(\frac{\partial^2\psi}{\partial x \partial v}\right)^2$.

In the second place these points of intersection will have the same significance for the course of the curves $\left(\frac{\partial\psi}{\partial x}\right)_v = q =$ constant, as the points of intersection $\frac{\partial^2\psi}{\partial v^2} = 0$ and $\frac{\partial^2\psi}{\partial x \partial v} = 0$ have for the course of the curves $\left(\frac{\partial\psi}{\partial v}\right)_x = -p =$ constant. The first point of intersection will be a double-point for the q lines, whereas the other point of intersection will present itself as an isolated point, the centre of detached closed portions of the q lines.

In the third place there will be a limiting temperature for the existence of the locus $\frac{\partial^2\psi}{\partial x^2} = 0$. With increasing value of T this curve contracts to an isolated point, just as is the case with $\frac{\partial^2\psi}{\partial v^2} = 0$ with maximum T_k, or as the curve $\frac{\partial^2\psi}{\partial v^2} = 0$ has a double point with minimum T_k.

In the fourth place there is a temperature at which the curves $\frac{\partial^2\psi}{\partial x^2} = 0$ and $\frac{\partial^2\psi}{\partial x \partial v} = 0$ only touch, and the two points of intersection have, accordingly, coincided.

And finally, and this is the most important case, there is a tem-

perature at which the intersection of these curves takes place in such a way that at one of the points of intersection a tangent may be drawn to $\frac{\partial^2\psi}{\partial x^2}=0$, for which $\frac{dv}{dx}=0$.

To determine these circumstances we have the three equations $\frac{\partial^2\psi}{\partial x^2}=0$, $\frac{\partial^2\psi}{\partial x\partial v}=0$ and $\frac{\partial^3\psi}{\partial x^3}=0$ and this problem proves to be the analogue of that mentioned above, for which $\frac{\partial^2\psi}{\partial v^2}=0$, $\frac{\partial^2\psi}{\partial x dv}=0$ and $\frac{\partial^3\psi}{\partial v^3}=0$. If there $\frac{dv}{dx}$ was $=\infty$, now $\frac{dx}{dv}=\infty$ or $\frac{dv}{dx}=0$.

So if the 3 equations $\frac{\partial^2\psi}{\partial x^2}=0$, $\frac{\partial^2\psi}{\partial x\partial v}=0$ and $\frac{\partial^3\psi}{\partial x^3}=0$ admit of a solution, the circumstances may be realised in which at the plaitpoint a tangent may be drawn / x-axis. Neglecting the variability of b with v we find for the three equations:

$$\frac{\partial^2\psi}{\partial x^2}=\frac{MRT}{x(1-x)}+\frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^2}-\frac{\frac{d^2a}{dx^2}}{v}=0 \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{\partial^3\psi}{\partial x^3}=-\frac{MRT(1-2x)}{x^2(1-x)^2}+2\frac{MRT\left(\frac{db}{dx}\right)^3}{(v-b)^3}=0 \quad . \quad . \quad (2)$$

$$\frac{\partial^2\psi}{\partial x\partial v}=\frac{MRT\frac{db}{dx}}{(v-b)^2}-\frac{\frac{da}{dx}}{v^2}=0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we put $a=A+2Bx+Cx^2$ and $b=b_1+x\beta=b_1+x(b_2-b_1)$ we get the equation:

$$\sqrt[3]{\frac{2x^2}{1-3x+2x^2}}=\tfrac{1}{2}\frac{C_x}{B+Cx}\left\{1\pm\sqrt{\left[1+\frac{4(B+Cx)(Cb_1-\beta B)}{C^2x\beta(1-x)}\right]}\right\}$$

If $B=a_{12}-a_1$ should be small in comparison with $a_1+a_2-2a_{12})x=Cx$, we get x equal to $^1/_3$ by approximation, at least if $\frac{b_1}{\beta}$ is aiso small.

Then real values are found both for x and for T and v; only this value of T can lie below the melting point in many cases, and consequently it cannot be observed.

However, I shall not enter into a further discussion. I will only point out, that for suitable values of T the curve $\frac{\partial^2\psi}{\partial x^2}=0$ represents a closed curve, which contracts with increasing value of T, and may contract into a point.

In the problem, for which $\frac{dv}{dx} = \infty$ at the plaitpoint, this case is the transition for the cases where $\frac{dv}{dx}$ is positive or negative. In the same way in the problem for which $\frac{dv}{dx} = 0$ in the plaitpoint, this is a transition case between $\frac{dv}{dx}$ positive or negative. So the cases may also exist for which on the side of the small volumes, the quantity $\frac{dv}{dx}$ in the plaitpoint may have reversed sign.

When we examine the shape of the curves $\frac{\partial^2\psi}{\partial x \partial v} = 0$ and $\frac{\partial^2\psi}{\partial x^2} = 0$, it appears that it is required for the realisation of the case, that when $\frac{db}{dx}$ is positive, also $\frac{da}{dx}$ and $\frac{d^2a}{dx^2}$ are positive, and that the calculated temperature must lie above T_k of the first component when we want to apply the result to the coexistence of gas and liquid phases.

At the top we have the limiting case of two coexisting phases. If the tangent is // x-axis, the molecular volume is equal and the density will be proportional to $m_1(1-x) + m_2 x$.

Put

$$d = \frac{m_1(1-x) + m_2 x}{v} \text{ and } d' = \frac{m_1(1-x') + m_2 x'}{v} \text{ and } d'-d = \frac{(m_2-m_1)(x'-x)}{v}.$$

When (m_2-m_1) and $(x'-x)$ have the same sign, $d'-d$ is positive. As $x'-x$ is negative when the first component has the smallest size of molecule, m_2-m_1 must also be negative, which is satisfied for helium and hydrogen.

We can, in general, represent the limiting density of a substance by $\frac{m}{b}$, and then the law would hold: When the most volatile substance has the greatest limiting density, the gas phase can be specifically heavier than the liquid phase. For Helium the limiting density is probably equal to that of the heavy metals. From the supposition that it is formed by splitting off from heavy metals this follows already with a certain degree of probability.

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[1]) On further investigation it has appeared to me that a point that satisfies the equations $\frac{\partial^2\psi}{\partial x^2} = 0$, $\frac{\partial^2\psi}{\partial x \partial v} = 0$, and $\frac{\partial^3\psi}{\partial x^3} = 0$, possesses the analytical character of a plaitpoint, but at least in many cases, does not behave practically as such. I hope to show this before long. (Added in the English translation).

Mathematics. — "*The rule of Neper in the four dimensional space.*" By Dr. W. A. Wythoff). (Communicated by Prof. P. H. Schoute.

(Communicated in the meeting of December 29, 1906).

1. The wellknown "rule of Neper" can in principle be formulated as follows:

If we regard as elements of a spherical triangle $A_1 A_2 A_3$, rectangular in A_2, the two oblique angles A_1 and A_3 the hypothenuse a_2 and the complements of the two other sides $\frac{1}{2}\pi - a_1$ and $\frac{1}{2}\pi - a_3$ [1]) we can apply to each formula generally holding for the rectangular spherical triangle the cyclic transformation

$$(A_3,\quad \tfrac{1}{2}\pi - a_3,\quad a_2,\quad \tfrac{1}{2}\pi - a_1,\quad A_1)$$

without its ceasing to hold.

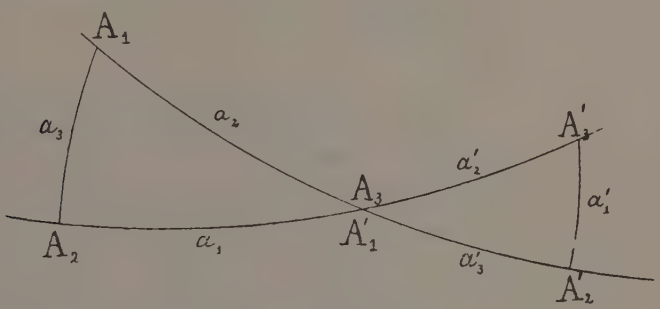

Fig. 1.

We prove this rule by prolonging the sides $A_1 A_3$ and $A_2 A_3$ which (Fig. 1) for convenience'sake we shall imagine as $< \frac{1}{2}\pi$, through the vertex $A_3 = A'_1$ with segments $A'_1 A'_2$ and $A'_1 A'_3$ so that $A_1 A'_2 = A_2 A'_3 = \frac{1}{2}\pi$. The spherical triangle $A'_1 A'_2 A'_3$ then proves to be again rectangular, namely in A'_2, whilst furthermore between the elements of both spherical triangles the following relations prove to exist:

$$A'_3 = \tfrac{1}{2}\pi - a_3 \quad ; \quad \tfrac{1}{2}\pi - a'_3 = a_2 \quad ; \quad a'_2 = \tfrac{1}{2}\pi - a_1 ;$$
$$\tfrac{1}{2}\pi - a'_1 = A_1 \quad ; \quad A'_1 = A_3.$$

From this is evident that the above mentioned cyclic transformation can be applied to the elements of each rectangular spherical triangle without their ceasing to be the elements of a possible rectangular

1) These are the complements of what Neper himself calls the "quinque circulares partes" of the rectangular spherical triangle. See N. L. W. A. Gravelaar, John Napier's werken, Verh. K. A. v. W., First section, vol. VI, N°., 6, page 40.

spherical triangle, from which further the rule of NEPER immediately follows.

The train of thoughts followed here will be found back entirely in the following.

2. A hyperspherical tetrahedron I shall call *doublerectangular*, if two opposite edges stand each normal to one of the faces.

Let us suppose the letters A_1, A_2, A_3 and A_4 at the vertices of the tetahedron in such a manner that $A_1 A_2$ is perpendicular to the face $A_2 A_3 A_4$ and $A_3 A_4$ perpendicular to the face $A_1 A_2 A_3$.

To make the tetrahedron doublerectangular it is necessary and sufficient for the angles of position on the edges $A_1 A_3$, $A_2 A_4$ and $A_2 A_3$ to be right: [1])

$$\alpha_{24} = \alpha_{13} = \alpha_{14} = \tfrac{1}{2}\pi ;$$

from which then ensues:

$$A_{23} = A_{24} = A_{32} = A_{31} = \tfrac{1}{2}\pi ,$$
$$A_{21} = \alpha_{34} ,$$
$$A_{34} = \alpha_{12} .$$

If we do not count the rectangular elements and if we count those which are equal only once the doublerectangular hyperspherical tetrahedron has 15 elements, namely α_{12}, α_{13}, α_{14}, α_{23}, α_{24}, α_{34}, α_{12}, α_{23}, α_{34}, A_{12}, A_{13}, A_{14}, A_{41}, A_{42}, A_{43}.

3. We now form, starting from a doublerectangular hyperspherical tetrahedron $A_1 A_2 A_3 A_4$ of which we think the edges all $< \tfrac{1}{2}\pi$, a second hyperspherical tetrahedron (Fig. 2) by prolonging the edges meeting in $A_4 = A'_1$ through this vertex, namely the edge $A_1 A_4$ with a segment $A'_1 A'_2$, the edge $A_2 A_4$ with $A'_1 A'_3$ and the edge $A_3 A_4$ with $A'_1 A'_4$, so that $A_1 A'_2 = A_2 A'_3 = A_3 A'_4 = \tfrac{1}{2}\pi$.

By very simple geometrical considerations we find that the tetrahedron $A'_1 A'_2 A'_3 A'_4$ is again doublerectangular, that namely $A'_1 A'_2$ is perpendicular to $A'_2 A'_3 A'_4$ and $A'_3 A'_4$ perpendicular to $A'_1 A'_2 A'_3$; furthermore it is evident that the following relations exist between

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[1]) The signs used here I have derived from Prof. Dr. P. H. SCHOUTE, Mehrdimensionale Geometrie, 1st vol., page 267, Sammlung SCHUBERT XXXV, Leipzig, G. J. GÖSCHEN, 1902.

So I understand

by α_{12} the edge $A_1 A_2$;

by α_{12} the angle of position formed by the faces lying opposite the vertices A_1 and A_2, i. e. the angle of position on the edge $A_3 A_4$;

by A_{12} the facial angle having A_1 as vertex and lying in the face opposite A_2, i. e. the angle $A_3 A_1 A_4$.

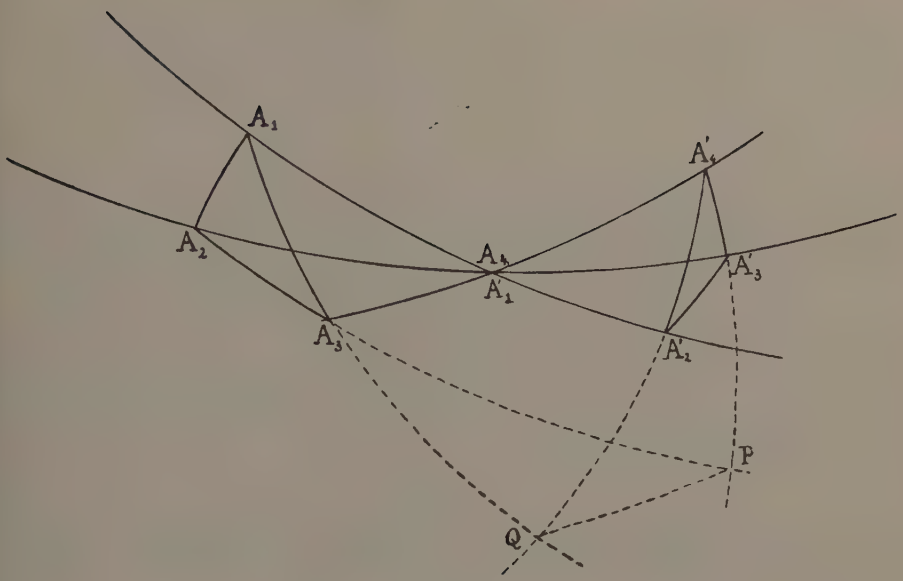

Fig. 2.

the elements of the two tetrahedra

$$\begin{aligned}
\tfrac{1}{2}\pi - a'_{12} &= a_{14} \ , \\
a'_{14} &= \tfrac{1}{2}\pi - a_{34} \ , \\
\tfrac{1}{2}\pi - a'_{34} &= a_{34} \ , \\
a'_{34} &= a_{23} \ , \\
a'_{23} &= a_{12} \ , \\
a'_{12} &= \tfrac{1}{2}\pi - a_{12} \ ; \\
A'_{14} = A_{43} \ &, \text{ i. e. } (\tfrac{1}{2}\pi - A'_{14}) + A_{43} = \tfrac{1}{2}\pi \ , \\
A'_{43} + a_{13} &= \tfrac{1}{2}\pi \ , \\
a'_{13} + a_{24} &= \tfrac{1}{2}\pi \ , \\
a'_{24} + A_{12} &= \tfrac{1}{2}\pi \ , \\
A'_{12} = A_{41} \ &, \text{ i. e. } A'_{12} + (\tfrac{1}{2}\pi - A_{41}) = \tfrac{1}{2}\pi \ , \\
A'_{41} + A_{14} = \tfrac{1}{2}\pi \ &^{1}), \text{ i. e. } (\tfrac{1}{2}\pi - A'_{41}) + (\tfrac{1}{2}\pi - A_{14}) = \tfrac{1}{2}\pi \ ; \\
A'_{42} &= \tfrac{1}{2}\pi - a_{23} \ , \\
\tfrac{1}{2}\pi - a'_{23} &= A_{13} \ , \\
A'_{13} &= A_{42} \ .
\end{aligned}$$

4. So if we regard instead of a_{12}, a_{34}, A_{14}, A_{41} and a_{23} their complements as elements of the tetrahedron, then the elements of the

1) In giving the proof of this we must remember that $A'_4 A'_3$ and $A_2 A_3$ lie on a sphere and therefore cut each other in a point P, just as $A'_4 A'_2$ and $A_1 A_3$ cut each other in a point Q.

doublerectangular hyperspherical tetrahedron can be arranged in three cycles, two of 6 and one of 3 elements, namely

1. $(\frac{1}{2}\pi - a_{12}, a_{14}, \frac{1}{2}\pi - a_{34}, a_{32}, a_{23}, a_{12})$,
2. $(\frac{1}{2}\pi - A_{14}, A_{43}, a_{13}, a_{24}, A_{12}, \frac{1}{2}\pi - A_{41})$,
3. $(A_{43}, \frac{1}{2}\pi - a_{23}, A_{13})$,

so that it is possible to allow the elements of each cycle to undergo all simultaneously a cyclic transformation, if only afterwards those of the second cycle are replaced by their complements,[1]) without these elements ceasing to be the elements of a possible doublerectangular hyperspherical tetrahedron.

These same simultaneous transformations may thus be applied to each formula holding in general for elements of the doublerectangular hyperspherical tetrahedron.

5. If we again apply the construction described in § 1 to the newly formed spherical triangle, etc. we find a closed range of five spherical triangles of which the hypothenusae form a spherical pentagon.

The sides of these five spherical triangles are parts of five great circles on the sphere, namely the circles part of which is formed by the three sides of the original spherical triangle and the two polar circles of the vertices of its oblique angles. These five great circles form, however, another second similar range of five spherical triangles, namely that of the opposite triangles of the former range.

6. We can likewise deduce in a manner indicated in § 3 out of a doublerectangular hyperspherical tetrahedron a range of such tetrahedra of which the faces all belong to six spheres, namely the spheres part of which is formed by the faces of the original tetrahedron and the polar spheres of the points A_1 and A_4.

Let us call B_1 the polar sphere of A_1, B_2 that of A_4, B_3 the sphere $A_1 A_2 A_3$, B_4 the sphere $A_4 A_1 A_2$, B_5 the sphere $A_3 A_4 A_1$ and B_6 the sphere $A_2 A_3 A_4$.

Each of these spheres divides the hypersphere into two halves of which I shall designate the one to which the original tetrahedron

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[1]) If we write the second cycle

$$(\tfrac{1}{2}\pi - A_{14}, \tfrac{1}{2}\pi - A_{43}, a_{13}, \tfrac{1}{2}\pi - a_{24}, A_{12}, A_{41})$$

or

$$(A_{14}, A_{43}, \tfrac{1}{2}\pi - a_{13}, a_{24}, \tfrac{1}{2}\pi - A_{12}, \tfrac{1}{2}\pi - A_{41}),$$

then no replacement of the elements by their complements is necessary, but the cycle has lost its symmetry with respect to the tetrahedron.

belongs by +, the other by —. The following list then indicates on which side of each of the six spheres the successive tetrahedra I, II, etc. are situated and by which they are limited. For the non-limiting spheres the sign has been placed in brackets.

	B_1	B_2	B_3	B_4	B_5	B_6
I	(+)	(+)	+	+	+	+
II	+	(+)	(+)	—	—	—
III	—	+	(+)	(—)	+	+
IV	+	—	+	(—)	(+)	—
V	—	+	—	—	(+)	(—)
VI	(—)	—	+	+	+	(—)
VII	(—)	(—)	—	—	—	—
VIII	—	(—)	(—)	+	+	+
IX	+	—	(—)	(+)	—	—
X	—	+	—	(+)	(—)	+
XI	+	—	+	+	(—)	(+)
XII	(+)	+	—	—	—	(+)
I	(+)	(+)	+	+	+	+

It is clear that the tetrahedra I and VII are opposite to each other, likewise II and VIII, III and IX, etc., whilst the tetrahedron I again follows tetrahedron XII.

Thus the whole range consists of 12 tetrahedra which are two by two opposite to each other, in contrast to what we found in the three-dimensional space, where *two* ranges of spherical triangles are formed of which one contains the triangles opposite to those of the other.

7. Between the volumes of each pair of tetrahedra belonging to the range exists a simple relation.

If we call V_I the volume of the first tetrahedron then the relation:

$$dV_I = \tfrac{1}{2}\, a_{12}\, da_{34} + \tfrac{1}{2}\, a_{14}\, da_{23} + \tfrac{1}{2}\, a_{34}\, da_{12}$$

holds for each variation of the tetrahedron remaining doublerectangular (thus a_{12}, a_{34} and a_{14} not changing).

Likewise

$$dV_{II} = \tfrac{1}{2}\,(\tfrac{1}{2}\pi - a_{14})\, da_{23} + \tfrac{1}{2}\,(\tfrac{1}{2}\pi - a_{34})\, da_{12} - \tfrac{1}{2}\,(\tfrac{1}{2}\pi - a_{34})\, da_{12}\,.$$

So therefore

$$V_I + I_{II} = \tfrac{1}{4}\pi a_{23} + \tfrac{1}{4}\pi a_{12} - \tfrac{1}{2} a_{12}(\tfrac{1}{2}\pi - a_{34}) + \text{constant.}$$

The constant is found by putting a_{12} equal to $a_{23} = a_{34} = a_{12} = \frac{1}{2}\pi$, in which case V_I takes up the sixteenth part of the whole hypersphere, i. e. $\frac{1}{8}\pi^2$, whilst V_{II} becomes $= 0$.

The constant then proves to be $-\frac{1}{8}\pi^2$, hence

$$V_I + V_{II} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi a_{12} + \tfrac{1}{4}\pi a_{23} - \tfrac{1}{2} a_{12}(\tfrac{1}{2}\pi - a_{34}).$$

Likewise we find.

$$V_{II} + V_{III} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi(\tfrac{1}{2}\pi - a_{12}) + \tfrac{1}{4}\pi a_{12} - \tfrac{1}{2}(\tfrac{1}{2}\pi - a_{14})(\tfrac{1}{2}\pi - a_{23}),$$
$$V_{III} + V_{IV} = -\tfrac{1}{8}\pi^2 + \tfrac{1}{4}\pi a_{14} + \tfrac{1}{4}\pi(\tfrac{1}{2}\pi - a_{12}) - \tfrac{1}{2} a_{34}(\tfrac{1}{2}\pi - a_{12}), \text{ etc.}$$

Every time the sum of the volumes of two successive tetrahedra can be expressed by means of four successive elements of the first cycle mentioned in § 4. We deduce easily from this:

$$V_I - V_{III} = \tfrac{1}{2} a_{12} a_{34} - \tfrac{1}{2} a_{14}(\tfrac{1}{2}\pi - a_{23}),$$

whilst in like manner we can find $V_{II} - V_{IV}$, $V_{III} - V_V$, etc. Further we find

$$V_I + V_{IV} = \tfrac{1}{2} a_{14} a_{23} - \tfrac{1}{2} a_{34}(\tfrac{1}{2}\pi - a_{12}) - \tfrac{1}{2} a_{12}(\tfrac{1}{2}\pi - a_{34})$$

and in like manner $V_{II} + V_V$, etc.

If we remember that the tetrahedra I and VII are alike with respect to their elements and volumes, II and VIII also, etc. and that with respect to the volumes we have to deal with only a closed range of six terms we see that of each arbitrary pair always either the sum or the difference of the volumes can be expressed in a simple manner.

Mathematics. — *"The locus of the cusps of a threefold infinite linear system of plane cubics with six basepoints."* By Prof. P. H. Schoute.

In the generally known representation of a cubic surface S^3 on a plane α to the plane sections of S^3 correspond the cubics through six points in α; here to the parabolic curve s^{12} of S^3 answers the locus C^{12} of the cusps of the linear system of those cubics. The principal aim of this short study is to deduce from wellknown properties of s^{12} properties of c^{12} and reversely.

1. If a plane rotates around a right line l of S^3 the points of intersection of that line l with the completing conic describe on l an involution, the double points of which are called the asymptotic points of l. According to the condition of reality of these asymptotic

points the 27 right lines of S^3, supposed to be real, are to be divided into two groups, into a group of 12 lines with imaginary asymptotic points, the lines

$$\begin{vmatrix} a_1 & a_2 & a_3 & a_4 & a_5 & a_6 \\ b_1 & b_2 & b_3 & b_4 & b_5 & b_6 \end{vmatrix}$$

of a doublesix and into a group of 15 lines $c_{12}, c_{13}, \ldots, c_{56}$ with real asymptotic points. If to the six basepoints A'_i of the linear system of the cubics the six lines a_i correspond — and this case we shall in the following continually have in view — then to the six lines b_i correspond the six conics b'^2_i through all the basepoints except A'_i and to the fifteen lines c_{ik} correspond the connecting lines $c'_{ik} = (A'_i, A'_k)$, whilst to the systems of conics (a^2_i) in planes through a_i, (b^2_i) in planes through b_i, (c^2_{ik}) in planes through c_{ik} correspond successively the pencils of the curves of the linear system with A'_i as doublepoint, the lines (b'_i) through A'_i and the conics (c'^2_{ik}) through the four basepoints differing from A_i and A_k. The situation of the six points A'_i is then such that each of the fifteen lines c'_{ik} is touched in real points by two conics of the pencils (c'^2_{ik}), whilst on the other hand the points of contact of the tangents out of the points A'_i to the conics b'^2_i are imaginary so that each point A'_i lies within the conic b'^2_i with the same index.

2. As a matter of fact all real points of a line l of S^3 are hyperbolic points of this surface with the exception of the two asymptotic points of this line showing a parabolic character; whilst each of these asymptotic points is point of contact of l with a conic lying on S^3, l touches in both points the parabolic curve S^{12}. If we apply this to each of the six lines a_i, imaged in the points A'_i, and if we consider that to a definite point P of a_i corresponds the point P' lying infinitely close to A'_i connected with A'_i by a line of definite direction (Versl., vol. I, pag. 143) we find immediately:

"The six basepoints A'_i of the linear system are fourfold points of the curve c^{12} of a particular character, consisting of the combination of two real cusps with conjugate imaginary cuspidal tangents, the cuspidal tangents of the curves out of the system with a cusp in A'_i".

The twelve points of intersection of the line c'_{ik} with c^{12} consist of the isolated points A'_i, A'_k counting four times and the real points

of contact with two conics out of the pencil (c'^2_{ik}) counting two times. Likewise do the 24 points of intersection of the conic b'^2_i with c^{12} consist of the five basepoints differing from A'_i counting four times and the imaginary points of contact with the tangents through A'_i counting two times.

3. From the investigations of F. KLEIN and H. G. ZEUTHEN dating from 1873 and 1875 it has become evident that the surface S^3 with 27 real right lines has ten openings and the parabolic curve s^{12} has ten oval branches. In connection with this we find:

"The locus c^{12} has ten oval branches."

We ask which situation of the six basepoints A'_i corresponds to the particular case of the "surface of diagonals" of CLEBSCH, in which the ten oval branches of the curve s^{12} have contracted to isolated points. In this case the fifteen lines with real asymptotic points, i.e. in our case the lines c'_{ik}, pass ten times three by three through a point; this is satisfied by the six points consisting of the five vertices of a regular pentagon and the centre of the circumscribed circle.

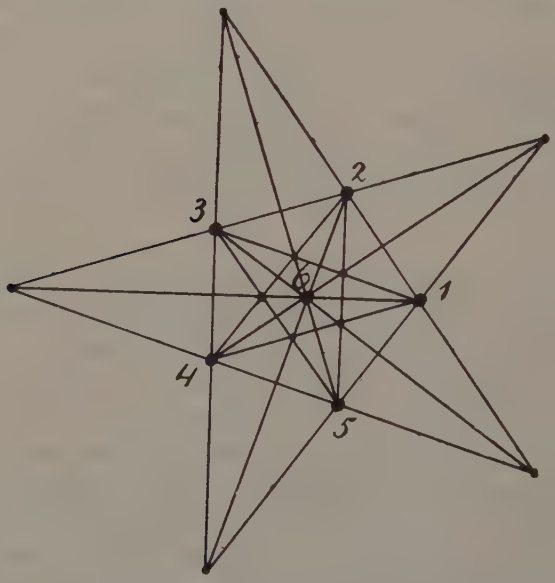

Fig. 1.

What is more, each six points having the indicated situation can be brought by central projection to this more regular shape. The ten meeting-points of the triplets of lines then form the vertices of two regular pentagons (fig. 1). The curve c^{12} corresponding to these six basepoints then consists of merely isolated points, namely of fourfold

points in the six basepoints and twofold points in the ten meeting points of the triplets of lines.

The remark that the curve c^{12} belonging to the six basepoints of fig. 1 has the line c'_{16} as axis of symmetry and transforms itself into itself when rotating 72° around A'_6, enables us to deduce in a simple way its equation with respect to a rectangular system of coordinates with A'_6 as origin and c'_{16} as x-axis. The forms which pass into themselves by the indicated rotation are

$$\varrho^2 = x^2 + y^2,\ P = x^5 - 10x^3y^2 + 5xy^4,\ Q = 5x^4y - 10x^2y^3 + y^5.$$

If we pay attention to the axis of symmetry and to the identity $P^2 + Q^2 = \varrho^{10}$ the indicated equation can be written in the form

$$\varrho^4 + a\varrho^6 + b\varrho^8 + c\varrho^{10} + d\varrho^{12} + P(e + f\varrho^2 + g\varrho^4 + h\varrho^6) + P^2(i + k\varrho^2) = 0,$$

so that we have to determine only the ten coefficients $a, b, \ldots, k$. If now the common distance of the points $A'_1, A'_2, \ldots, A'_5$ to A'_6 is unity, then

$$x^4\left(x + \frac{3-e}{2}\right)^2 (x-1)^4 \left(x + \frac{3+e}{2}\right)^2 = 0,$$

where e stands for $\sqrt{5}$, represents the twelve points of intersection of the curve with the x-axis. By performing the multiplication this passes into

$$x^4(x^8 + 2x^7 - 7x^6 - 6x^5 + 20x^4 - 6x^3 - 7x^2 + 2x + 1) = 0.$$

From this follows

$$a = -7,\quad b = 20,\quad c + i = -7,\quad d + k = 1,$$
$$e = 2,\quad f = -6,\quad g = -6,\quad h = 2.$$

So the equation

$$\varrho^4 - 7\varrho^6 + 20\varrho^8 - 7\varrho^{10} + \varrho^{12} + 2P(1 - 3\varrho^2 - 3\varrho^4 + \varrho^6) - Q^2(i + k\varrho^2) = 0$$

is determined, with the exception of the coefficients i and k still unknown. Now the parallel displacement of the system of coordinates to A'_1 as origin furnishes a new equation, of which the form

$$(4 - i - k)y^2 + 2(12 - 4i - 5k)xy^2 + x^4 + (54 - 28i - 45k)x^2y^2 + (5 + 4i + 3k)y^4$$

represents, after multiplication by 25, the terms of a lower order than five. The new origin being a fourfold point of c^{12} and the terms with y^2 and xy^2 having thus to vanish, we find

$$i = 8\quad ,\quad k = -4,$$

on account of which the indicated form passes into

$$(x^2 + 5y^2)^2.$$

The correctness of this result is evident from the following. Just as the two tangents in the old origin counting two times are represented by $x^2 + y^2 = 0$, and therefore coincide with the tangents out of A'_6 to the conic through the other basepoints, so $x^2 + 5y^2 = 0$ represents

for the new origin A'_1 the pair of tangents out of A'_1 to the conic through the other basepoints. Or, if one likes, just as $x^2 + y^2$ is with the exception of a numerical factor, the fourth transformation ("Ueberschiebung") of the first member of the equation $Q = 0$ of the lines connecting A'_6 to the remaining basepoints, so $x^2 + 5y^2$ represents, likewise with the exception of a numerical factor, the fourth transformation of the first member of the equation $\frac{Py}{x} = 0$, which indicates with respect to the new origin A'_1 the five lines connecting A'_1 to the remaining basepoints.

Finally the equation of c^{12} is

$$\varrho^4(\varrho^8-7\varrho^6+20\varrho^4-7\varrho^2+1)+2P(\varrho^6-3\varrho^4-3\varrho^2+1)+4Q^2(\varrho^2-2)=0, \quad (1)$$

or entirely in polar coordinates (ϱ, φ)

$$4(\varrho^2-2)\varrho^5 \cos 5\varphi=(\varrho^2+1)(\varrho^4-4\varrho^2+1)\pm(\varrho^2-1)^2\sqrt{(\varrho^2-1)(4\varrho^2+1)(5\varrho^2-1)}. \quad (2)$$

It is easy to show that this curve admits of no real points differing from the six basepoints A'_i and the ten points of intersection of the triplets of connecting lines. If for brevity we write (2) in the form

$$L \cos 5\varphi = M \pm \sqrt{N},$$

then we find

$$-L^2 \sin^2 5\varphi = (M^2 + N - L^2) \pm 2M\sqrt{N} \quad . \quad . \quad . \quad (3)$$

and

$$\left.\begin{aligned} M^2+N-L^2 &\equiv 2(\varrho^2-1)^2(2\varrho^2-1)(\varrho^8-6\varrho^6+14\varrho^4+2\varrho^2-1) \\ (M^2+N-L^2)^2 - 4M^2N &\equiv 4\varrho^8(\varrho^2-1)^4(\varrho^2-2)^2(\varrho^4-7\varrho^2+1)^2 \end{aligned}\right\} \quad . \quad . \quad (4)$$

If now we moreover notice that N is negative and therefore $\cos 5\varphi$ complex when ϱ^2 lies between $\frac{1}{5}$ and 1, the following is immediately evident:

a. The first member of the second equation (4) tends to zero, when ϱ^2 assumes one of the values $0, 1, 2, \frac{1}{2}(7 \pm 3e)$; it is positive for all other values of ϱ^2.

b. If $\sqrt{N}$ is real and ϱ^2 differs from unity the second member of the first equation (4) is positive; for the equation

$$\varrho^8 - 6\varrho^6 + 14\varrho^4 + 2\varrho^2 - 1 = 0$$

has, as is evident when the roots ϱ^2 are diminished by $\frac{1}{2}$, besides *one* real negative root only *one* real positive one between $\frac{1}{5}$ and 1.

c. If ϱ^2 differs from $0, 1, 2, \frac{1}{2}(7 \pm 3e)$ the second member of

(3) is positive when N is positive, and therefore φ is imaginary.

d. Neither does $\varrho^2 = 2$ give a real value for φ; for substitution in (1) furnishes for $\cos 5\varphi$ the result $\frac{3}{4}\sqrt{2}$.

e. So we find only the real points:

$\varrho = 0$, φ indefinite . . . . . A'_6,

$\varrho = 1$, $\cos 5\varphi = 1$ . . . . . $A'_1, A'_2, A'_3, A'_4, A'_5$,

$\varrho = \frac{3 \pm e}{2}$, $\cos 5\varphi = -1$ . . . the ten points of intersection of the fifteen connecting lines three by three.

4. We now consider a second case, in which the position of the six basepoints is likewise a very particular one, where namely these points form the vertices of a complete quadilateral. Through these six points not one genuine cubic with a cusp passes. For the three pairs of opposite vertices (A_1, A_2), (B_1, B_2), (C_1, C_2) of a complete quadilateral (fig. 2) form on each curve of order three, containing

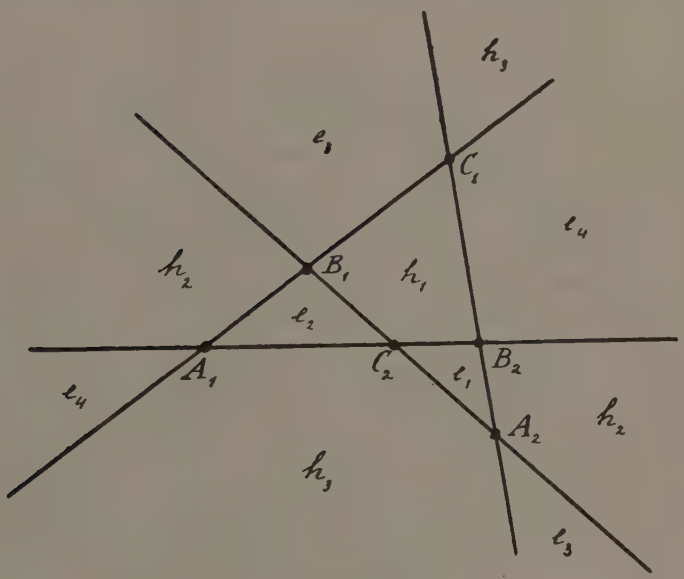

Fig. 2.

them, three pairs of conjugate points of the same system, and these do not occur on the cubic with a cusp, because through each point of such a curve only *one* tangent touching the curve elsewhere can be drawn. In this special case the locus of the cusps has broken

up into the four sides of the quadrilateral each of those lines counted three times. For it is clear that an arbitrary point of the line $A_1B_1C_1$ e. g., as a point of contact of this line with a conic passing through A_2, B_2, C_2, represents a cusp of the linear system of cubics. We can even expect that each of the four sides must be taken into account more than one time, because each of those points instead of being an ordinary cusp is a point, where two continuing branches touch each other. And finally the remark that the sides of the quadrilateral divide the plane into four triangles e with elliptic and three quadrangles h with four hyperbolic points, so that they continue to form the separation between those two domains, forces us to bring them an odd number of times into account, namely three times because we must arrive at a compound curve c^{12}.

Some more particulars with respect to the domains e and h. The nodal tangents of the cubic (fig. 3) passing through the three pairs of points (A_1, A_1), (B_1, B_2), (C_1, C_2) and having in P a node, are the double rays of the involution of the pairs of lines connecting

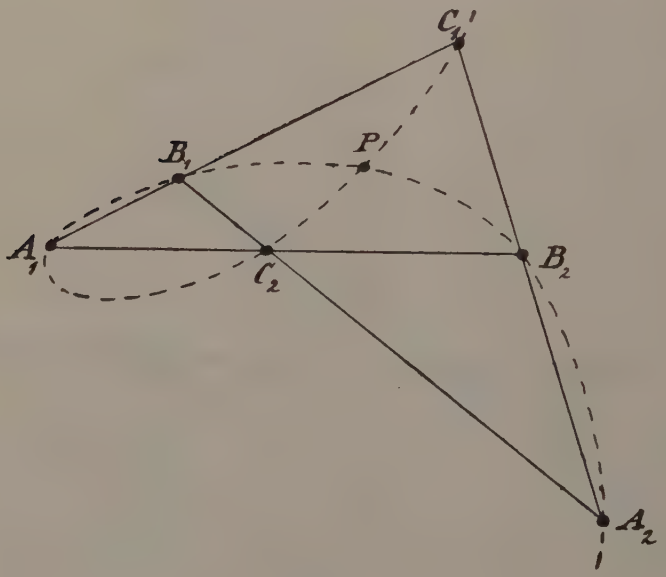

Fig. 3.

P with the three pairs of points mentioned, so also the tangents in P to the two conics of the tangential pencil with the sides of the quadrilateral as basetangents, passing through P; now, as these two conics are real or conjugate imaginary according to P lying in one

of the three quadrangles h or in one of the four triangles e, what was assumed follows immediately.

To the case treated here of c^{12} broken up into four lines to be counted three times corresponds the parabolic curve of the surface S^3 with four nodes.

5. In the third place we consider still the special case of six basepoints lying on a conic, in which the linear system of cubics contains a net of curves degenerating into a conic and a right line; in this net of degenerated curves the conic is ever and again the conic c^2 through the six basepoints and the right line is an arbitrary right line of the plane.

This case can in a simple way be connected with a surface S^3 with a node O. If we project this surface out of this node O on a plane α not passing through this point, then the plane sections of the surface project as cubics passing through the six points of intersection of α with the lines of the surface passing through O; because these six lines lie on a quadratic cone, the six points of intersection with α lie on a conic. Besides, the sections with planes through O project as right lines; therefore the completing conic c^2 must evidently be regarded as the image of the node O. Of course we must here again think that c^2 corresponds point for point to the points of O^3 lying at infinite short distance from O^3; for c^2 is the section of α with the cone of the tangents to S^3 in O.

As c^2 with one of its tangents represents a curve of the linear system, this conic belongs at least twice to the locus of the cusps. Here too this locus of cusps improper with continuing branches must be accounted for three times, so that the locus proper is a curve c^6 of order six, touching c^2 in the six basepoints.

Let us suppose that c^2 is a circle and that the six basepoints on that circle (fig. 4) form the vertices of a regular hexagon, then the curve c^6 has the shape of a rosette with six leaves having the centre O' of the circle and the points at infinite distance of the diameters A_1A_4, A_2A_5, A_3A_6 as isolated points. Of the ten ovals there are four contracted to points, whilst the six remaining ones have joined into the circle of the basepoints and the curve c^6.

If we take point O' as origin and the line $O'A_1$ as x-axis of a rectangular system of coordinates, then if $O'A_1$ is unity of length we find for the equation of c^6

$$4y^2(y^2 - 3x^2)^2 + 9(x^2 + y^2)^3 - 9(x^2 + y^2) = 0.$$

It is evident from this equation that the curve c^6 can really stand

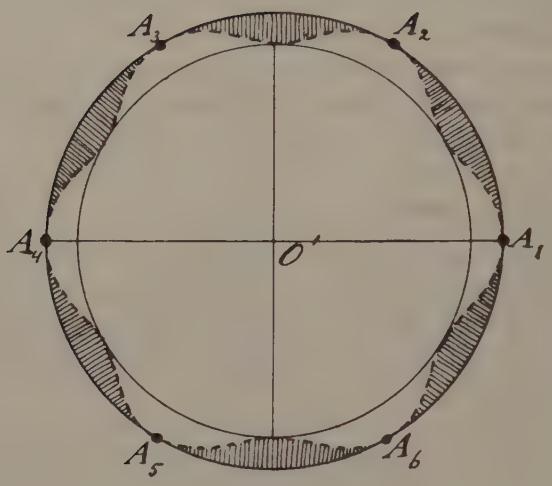

Fig. 4.

rotation of multiples of 60° round O', for then $x^2 + y^2$ and $y(y^2 - 3x^2$ are transformed into themselves.

Out of the equation

$$\sin 3\varphi = \pm \frac{3}{2r^3}\sqrt{1 - r^3}$$

on polar coordinates it is evident that the curve c^6 (with the exception of its four isolated points) is included between the circles described out of O' with the radii 1 and $\frac{1}{2}\sqrt{3}$.

If we pass from the locus of the cusps to the parabolic curve of S^3 we must notice that the last curve has the node O of S^3 as threefold point, because c^2 has separated itself three times from the locus c^{12}. So this parabolic curve is an s^9 of order nine, a result which will presently be arrived at in an other way.

We shall give — without wishing in the least to exhaust this case of the six basepoints situated on a conic — some degenerations of the remaining curve c^6 corresponding to some definite coincidences of the basepoints.

a) The cases (2, 2, 2), (4, 2), (6). If the six basepoints coincide two by two in three points of the conic, then c^6 consists of the sides of the triangle of the basepoints counted double, originating from compound cubics with a double line; there is not a locus proper. In reality the case (2, 2, 2) of a conic touching in three points cannot occur for a genuine cubic with a cusp.

The cases (4, 2) and (6) are to be regarded as included in the preceding. By allowing two of the vertices or the three vertices of the triangle just considered to coincide we find for case (4, 2) the connecting line of the two basepoints counted four times and the tangent to the conic in the basepoint of highest multiplicity counted two times, for case (6) the tangent to the conic in the point counting for six basepoints counted six times. That there can be no locus proper in the last case ensues also from the fact, that a genuine cubic with cusp allows of no sextactic point.

b) The case (3, 3). If the six basepoints coincide three by three in two points of the conic, then c^6 consists of a part improper, the connecting line of the two points counted four times, and a part proper, a conic touching the conic of the basepoints in these points. The new conic lies *outside* the conic of the basepoints.

c) The case (1, 5). This case agrees in many respects with the preceding. We find a part improper, the tangent in the point counting for five basepoints drawn to the conic of the basepoints, and a part proper, a conic touching the conic of the basepoints in these points. The new conic lies *inside* the conic of the basepoints.

6. Of course it is possible to call forth by the curve c^{12} successively all the different special cases which can put in an appearance by the parabolic curve s^{12} of the various surfaces S^3. As this would lead us here too far, we limit ourselves to a single remark, which can eventually facilitate an analytic investigation of this idea.

According to the general results with respect to a linear system of curves c^n obtained as early as 1879 by E. Caporali the locus $c^{4(2n-3)}$ of the cusps of this system has in each r-fold basepoint of the system a $4(2r-1)$ fold point and besides $6(n-1)^2-2\Sigma(3r^2-2r+1)$ nodes C. Each of those points C is characterized by the property that each curve of the system passing through this point is touched in this point by a definite line c.

For the case under observation, $n = 3$ of the cubics, the number of points C is represented by $24-6p$, when p is the number of basepoints.

If we wish to investigate analytically what peculiarity the locus of the cusps shows in a basepoint of the system, or how a line through three basepoints separates from it, then the result — and this is the remark indicated — will be independent of the fact, whether the remaining basepoints occur or not, if in the former case, that some of these basepoints appear in a real or in an imaginary condition, we assume that these points both with respect to each

other and to the former basepoints have not a particular position.

With the aid of this remark we can easily find the following theorems, with which we conclude:

"Both cusps of which the fourfold point of the curve c_{12} coinciding with a basepoint A'_i seems to consist and the two cusps of the curves of the system showing in this point a cusp, coincide in cuspidal tangents, but they turn their points to opposite sides."

"If the three basepoints A'_1, A'_2, A'_3 lie on a right line l, the locus proper of the cusps reduces itself to a curve c^9 touching the line l in A'_1, A'_2, A'_3. If the three remaining basepoints exist then the points of intersection of l with the sides of the triangle having those basepoints as vertices are points of c^9".

The last case answers to that of a surface S^3 with a double point; the parabolic curve having in this doublepoint a threefold point, because l separates itself three times from c^{12}, is as has been found above already a twisted curve of order nine.

Physics. — "*An investigation of some ultra-red metallic spectra.*" By W. J. H. Moll. (Communicated by Prof. W. H. Julius).

(Communicated in the meeting of December 29, 1906).

Among the spectra of known elements those of the alkali-metals, by their relatively simple structure, lend themselves particularly well to an investigation of their ultra-red parts. Many observers have consequently sought for emission lines of these metals in this region.

For the first part of the ultra-red spectrum the photographic plate may be sensitised; especially Lehmann [1]) measured in this way various lines with wave-lengths ranging to almost 1 μ. By means of the bolometer Snow [2]) could advance to 1.5 μ.

For the further region, however, nothing was known about these spectra. Coblentz [3]), to be sure, was led by a series of observations in this respect, to the conclusion that the alkali-metals emit no specific radiation beyond 1.5 μ, but I had reason to doubt the validity of this conclusion.

In what follows I will briefly describe the method by which some ultra-red spectra were investigated, and the lines thus found. In an

1) H. Lehmann. D.'s Ann. **5**, 633, 1901.

2) B. W. Snow. W.'s Ann. **47**, 208, 1892.

3) W. W. Coblentz. Investigations of Infra-red Spectra. Carnegie Inst. Washington. 1905.

academical thesis, which will soon be published, further details will be given.

For the investigation of the alkalies, the metallic salts were volatilised in the arc in the ordinary way. The very complicated band-spectrum, emitted by the arc when no metallic vapour is present, extends far into the ultra-red. But this interferes in no way with the investigation of the metals, since it is entirely superseded when the arc contains a sufficient quantity of metal. On the other hand the continuous spectrum, emitted by the incandescent particles in the arc, makes it somewhat difficult to observe some feebler lines; besides, the radiation of carbonic acid, the product of combustion of the carbons, (with a maximum near 4,44 μ) persists with almost unchanged intensity.

The image of the arc is projected by a concave mirror on the slit of a reflecting-spectrometer; the rays are analysed by a rock-salt prism and part of the so formed spectrum falls on a linear thermopile. This thermopile, like that of RUBENS, is built up of iron and constantan; all the dimensions were chosen smaller than in the original pattern and a great sensitiveness was obtained. As well the emitting slit as the thermopile are mounted in fixed positions; in order to throw on this latter different parts of the spectrum in succession, the prism can be rotated through small angles. A WADWORTH combination of prism and plane mirror maintains minimum-deviation during rotation.

In chosing and designing the instruments, the desirability was kept in mind of replacing the very tiring reading of the galvanometer and the simultaneous noting of the corresponding position of the prism, by an automatical recording-device. I had in mind the splendid arrangement by which LANGLEY has for years recorded the intensity-curve of the ultra-red solar spectrum on a photographic plate. That this method has not been followed for recording heat-spectra instead of the time-absorbing visual observations, must be ascribed in the first place to a very complicated mechanism being required for obtaining complete correspondence between the linear displacement of the photographic plate and the rotation of the spectrometer, and secondly to the difficulty of keeping the surrounding temperature perfectly equal during the observations.

With very simple means I devised a method of recording, which avoids these two difficulties, while yet it warrants a sure "correspondence", and yields accurate results also when changes in the surrounding temperature cannot be prevented. For this purpose the continuous recording has been replaced by the marking of a series

of dots, while for the continuous rotation of the spectrometer an intermittent one has been substituted. In this way for any recorded radiation-intensity the corresponding position of the prism can be found, not by *measuring* abscissae, but by *counting* dots. Since moreover not only the deflections of the galvanometer but each time also the zero-positions are recorded, it is possible to determine on the spectograms the radiation-intensities also when during the observations the surrounding temperature, and consequently the zero-position, was variable.

The principal advantages of this method of observation over the usual one are:

1. the absolute reliability of the observations,
2. the very short time required for a set of observations,
3. the accuracy with which interpolation is possible when the zero-position shifts,
4. the non-existence of disturbances, caused by the proximity of the observer,
5. the complete comparability of the different observations,
6. the possibility of estimating the probable error from the shape of the zero-line.

The short time in which a set of observations is made, is of importance when e.g. heat-sources are investigated which, like the arc, show slow changes in radiation-intensity. A spectrum, ranging from 0,7 to 6 μ was recorded with 200 displacements of the spectrometer in two hours.

In the spectrograms a spectral line is represented by 5 to 6 dots. With one displacement of the spectrometer namely the line is shifted over a distance amounting to $^2/_5$ of the breadth of the image of the slit, or of the equal breadth of the thermopile. Hence the same kind of radiation will strike the thermopile during five successive displacements. From the mutual position of the dots, the place where the radiation-intensity has its maximum may be accurately determined. In order to derive from this the place occupied by the line in the spectrum, it is sufficient to know one fixed point in the spectrum. This fixed point was as a rule taken from a comparison spectrum, for which the carbonic acid emission of a Bunsen flame was chosen, the maximum of which, according to very accurate measurements of PASCHEN, lies at 4.403 μ. Part of the flame spectrum was for this purpose recorded simultaneously with the spectrum to be studied.

A simple calculation then gives the refractive index for the unknown ray. In order to derive from this the wave-length of the line, a dispersion formula must be used. I became aware that the

well-known dispersion curves of LANGLEY and of RUBENS show considerable differences, and although at first sight LANGLEY's determinations seem to be much preferable, yet on closer examination their excellence must be doubted, especially for the longer wavelengths. To prefer one of the dispersion curves to the other seems to be at present a matter of arbitrary choice. So I have given in the tables besides the observed refractive indices, the wavelengths, calculated from them as well by LANGLEY's as by RUBENS' formula. The refractive indices hold good for a temperature of 20°; their determination is based on the index 1.54429 for the *D*-line, a value, derived from very accurate determinations by LANGLEY.

The tables given below contain the lines of Na, K, Rb and Cs (I have been unable to obtain reliable results with Li in the arc) and of Hg. The results were derived from a large number of spectrograms (10 to 12 for each metal). For the investigation of the mercury spectrum a mercury arc-lamp was devised, furnished with a rock-salt window. The spectrum of mercury has been repeatedly investigated as far as 10μ; no measurable emission has been found beyond 1.7μ.

In the tables the first column gives the refractive index n of rock-salt, the second and third the wave-length μ of the line, according to the formulae of LANGLEY and RUBENS, and the fourth the approximate value I of the intensity.

For the lines of which the exact position was difficult to ascertain, the refractive index is only given in four decimals.

SODIUM.

n	μ(Langley)	μ (Rubens)	I
1.53529	0.819	0.816	240
.53062	1.14	1.13	180
.52961	1.27	1.25	15
.5286	1.44	1.42	5
.5281	1.57	1.54	5
.52711	1.85	1.80	25
.52613	2.21	2.16	45
.52589	2.31	2.25	35
.52455	2.90	2.84	20
.5234	3.42	3.36	5
1.52178	4.06	4.00	10

POTASSIUM.

n	μ(Langley)	μ (Rubens)	I
1.53654	0.771	0.768	620
.5325	0.97	0.96	10
.5310	1.11	1.10	20
.53030	1.18	1.17	320
.52972	1.25	1.24	200
.52823	1.53	1.50	95
.5261	2.24	2.18	5
.52486	2.76	2.70	20
.52401	3.14	3.08	20
.52263	3.73	3.67	15
1.52184	4.04	3.98	10

RUBIDIUM.

n	μ(Langley)	μ (Rubens)	I
1.53733	0.744	0.742	12
.53624	0.782	0.779	450
.5359	0.795	0.792	300
.5332	0.93	0.92	10
.53202	1.01	1.00	35
.5309	1.11	1.10	10
.52912	1.35	1.33	200
.52830	1.49	1.51	180
.52597	2.28	2.22	20
.52477	2.80	2.73	25
1.52186	4.03	3.97	10

CAESIUM.

n	μ(Langley)	μ (Rubens)	I
1.53566	0.803	0.801	40
.53451	0.855	0.851	250
.53375	0.895	0.891	200
.5333	0.920	0.914	75
.53202	1.01	1.00	90
.52902	1.37	1.35	70
.52846	1.48	1.45	80
.5275	1.74	1.70	5
.5264	2.08	2.03	5
.5257	2.41	2.35	5
.52433	3.00	2.93	50
.52315	3.51	3.45	30
1.52203	3 97	3.91	10

MERCURY.

n	μ(Langley)	μ (Rubens)	I*
1.53198	1.01	1.00	28
.53076	1.13	1.11	8
.52907	1.36	1.34	11
.52828	1.52	1.49	5
1.52759	1.70	1.66	5

* The intensity of the green and yellow mercury lines has been put = 10.

Mathematics. — "*On the locus of the pairs of common points and the envelope of the common chords of the curves of three pencils.*" 2nd part.: *Application to pencils of conics.* By Dr. F. SCHUH. (Communicated by Prof. P. H. SCHOUTE.)

(Communicated in the meeting of December 29, 1906).

9. If the pencils of curves are pencils of conics ($r = s = t = 2$) then in the case of there being no common base-points the locus is of order fifteen and the envelope of class six. In the following we

wish to treat the case more closely, that one of the pencils has two points in common with each of the two others, where we shall attain at results in another way, which will prove to agree to the general ones and complete these in some parts.

Let $ABCD$, $ABEF$ and $CDGH$ be the three pencils of conics. On one conic of the pencil $ABCD$ the two other pencils describe two quadratic involutions of which the connecting lines of the pairs of points pass through a point K of EF, resp. a point L of GH. The pair of common points PP' of these two involutions is thus determined by the right line KL. If the conic $ABCD$ describes the whole pencil, K and L describe projective series of points on EF and GH. For, if we take K arbitrarily on EF, the conic $ABCD$ is determined by it, as it must pass through the second point of intersection of CK with the conic $ABEFC$ (as likewise through the second point of intersection of DK and the conic $ABEFD$); by the conic $ABCD$ the point L is unequivocally determined. Reversely to a point L of GH now corresponds one point K. The projective series of points are however in general not perspective; *so the line* KL *or* PP' *envelops a conic* N *touching* EF *and* GH.

Of that conic three other tangents are easy to construct, namely by taking for the conic $ABCD$ in succession each of the three degenerations. If that conic is $AB \,.\, CD$ then the movable points of intersection with conics of the pencil $ABEF$ lie on CD so that K lies on CD, thus in the point of intersection K_1 of CD and EF; likewise does L coincide with the point of intersection L_1 of AB and GH. The line K_1L_1 is thus tangent to N. The construction becomes a little less simple if we take one of the other degenerations e.g. $AC \,.\, BD$. By cutting this by the degenerated conic $AE \,.\, BF$ of pencil $ABEF$ it is evident that K coincides with the point of intersection of EF with the line connecting the point of intersection of AE and BD with the point of intersection of BF and AC; in similar manner L is found.

To the locus of the points P and P' belongs the locus of the points of intersection of the conics of the pencil $ABCD$ with the projectively related series of tangents KL of the conic N. This locus (as is easily evident out of the points of intersection with an arbitrary right line or with an arbitrary conic of the pencil $ABCD$) is of order five with double points in A, B, C and D; further it passes through E, F, G and H, as K coincides with E when the conic $ABCD$ passes through E, etc. If we take for the conic of the pencil $ABCD$ the degeneration $AB \,.\, CD$, then KL passes into K_1L_1 which line cuts the conic $AB \,.\, CD$ in the points K_1 and L_1, which thus

lie on the locus of the points of intersection too. By taking the two other degenerations we find four more points of C_5. Altogether there are 10 single and 4 double points by which C_5 is determined.

If we take the degeneration $AB \,.\, CD$, the particularity occurs, that the pair of points of the involution described by the pencil $ABEF$ can become indefinite on AB, if namely the conic $ABEF$ breaks up into $AB \,.\, EF$. By this the whole line AB (and of course the line CD too) will belong to the locus proper of P and P' [1]). To the part proper of the envelope of the lines PP' the pairs of points PP' lying on AB or CD contribute nothing but the lines AB and CD (which belong also to the part improper of the envelope, the points A, B, C and D), which does not give rise to a higher class.

So the locus proper of P and P' consists of the lines AB and CD and the curve C_5 and is thus in accordance to the general results of order seven. The line $AB\,(CD)$ intersects C_5 in the points A and B (C and D) to be counted double and in L_1 (K_1). *The curve C_7 has three double points differing from the base-points* (of which E, F, G and H are single and A, B, C and D threefold points of C_7) *namely K_1, L_1 and the point of intersection T of AB and CD.* These form a triplet of double points belonging together of which we spoke in § 5. The conics of the three pencils passing through one of those double points, also pass through the two others; these conics are $AB \,.\, CD$, $AB \,.\, EF$ and $CD \,.\, GH$. To the branches TK_1 and TL_1 of C_7 passing through T correspond respectively the branches K_1T and L_1T passing through K_1 and L_1, whilst the branches of C_5 passing through K_1 and L_1 correspond mutually.

Summing up we find:

For the conics $ABCD$, $ABEF$ and $CDGH$ the locus proper of the pairs of common points PP' consists of the lines AB and CD and a curve of order five, having in A, B, C and D double points and in E, F, G and H single points and further passing through the point of intersection K_1 of CD and EF and the point of intersection L_1 of AB and GH. The envelope proper of the lines PP' is a conic touching the lines EF, GH and K_1L_1.

10. *If the points A, B, C, D, E and F lie on a conic,* the latter then belongs to the locus, so that the C_5 breaks up into that conic and a C_3 passing through A, B, C, D, G, H, K_1 and L_1. To each conic of the pencil $ABCD$ now belongs the same point K, namely K_1, as is immediately evident when we make the conic of

[1]) More generally: if two base-points of one pencil lie with two base-points of another pencil on a right line, that line belongs to the locus proper.

the pencil $ABEF$ to pass through C and D. If we take $ABCDEF$ for the conic of the pencil $ABCD$, then K is indefinite on EF, whilst point L is to be found somewhere in L_2 on GH. The correspondence between the points K and L is of such a kind that to a point L differing from L_2 the same point K always corresponds, namely K_1, whilst when L coincides with L_2 point K is arbitrary on EF. *So the conic N breaks up into the two points K_1 and L_2.* The relation between the conics of the pencil $ABCD$ and the tangents KL or PP' of N is of such a kind, that to the conic $ABCDEF$ every line through L_2 corresponds and that, for the rest, between the conics $ABCD$ and the lines through K_1 a projective relation exists, in which to the conics $ABCDEF$, $ABCDG$, $ABCDH$ and the degenerated conic $AB \,.\, CD$ respectively K_1L_2, K_1G, K_1H and K_1L_1 correspond. From this is also evident, that *the curve C_5 breaks up into the conic $ABCDEF$ and a C_3 passing through A, B, C, D, G, H, K_1 and L_1* and farther that *C_3 passes through the points of intersection of K_1L_2 with the conic $ABCDEF$.*

The double points of $C_7 = AB \,.\, CD \,.\, ABCDEF \,.\, C_3$ differing from the base-points are K_1, L_1, T and the two points of intersection of K_1L_2 with $ABCDEF$. The latter two doublepoints do not furnish a triplet of points through which conics of the three pencils pass, but two coinciding pairs of points; the branches through one doublepoint correspond to the branches through the other and, it goes without saying, in such a way that the branches belonging to C_3 correspond mutually and likewise the branches belonging to the conic $ABCDEF$.

11. *If moreover the points A, B, C, D, G and H lie on a conic,* C_3 breaks up into that conic and the line K_1L_1 (L_2 then coincides with L_1) *so that the locus proper then consists of the conics $ABCDEF$ and $ABCDGH$ and the lines AB, CD and K_1L_1.* When conic $ABCD$ does not pass through E, and F neither through G and H, the point K coincides with K_1 and L with L_1; so that the pair of points PP' lying on that conic is always determined by the same line K_1L_1. Hence K_1L_1 forms part of the locus. The C_7 has now seven double points differing from the base-points, namely one triplet K_1, L_1, T, and two pairs, the two points of intersection of K_1L_1 with the conic $ABCDEF$ and those with the conic $ABCDGH$.

If the point K_1 coincides with L_1 and therefore also with T, i.o.w. *if the four lines AB, CD, EF and GH pass through one point,* on each conic of the pencil $ABCD$ the two involutions coincide. *The locus proper then becomes indefinite. If we bring through an arbi-*

trary point P a conic of each of the pencils, then those conics have another second common point, namely the second point of intersection of the line TP with the conic $ABCDP$. The envelope proper is then still definite and consists of two coinciding points T.

12. *If the points E and G coincide,* then if the conic of the pencil $ABCD$ passes through E the point K as well as the point L coincides with E. The series of points K and L are perspective, the lines KL all pass through a selfsame point U.

The conic N breaks up into two points E and U. As E belongs to the part improper of the envelope, *the envelope proper now consists only of point U.* By taking for the conic of the pencil $ABCD$ the degeneration $AB \,.\, CD$ it is evident that U lies on the line $K_1 L_1$. Another line KL and by that the point U itself can be constructed in the way indicated in § 9 by allowing the conic $ABCD$ to break up into $AC \,.\, BD$ or $AD \,.\, BC$.

Between the lines KL or PP' through U and the conics of the pencil $ABCD$ exists a projective correspondence, where to the conics $ABCDE$, $ABCDF$, $ABCDH$ and $AB \,.\, CD$ respectively the lines UE, UF, UH and $K_1 L_1$ correspond. *The locus of the points of intersection is a cubic through the points $A, B, C, D, U, E, F, H, K_1$ and L_1,* which is determined by these 10 points; the third points of intersection of that curve with AC, AD, BC and BD are easy to construct.

On the conic $ABCDE$ the two involutions coincide, so that that conic has separated from the C_5 of § 9 and has become improper.

The locus proper consists now of the lines AB and CD and the above-named C_3, so it is of order five. Differing from the base-points the C_5 has three double points, K_1, L_1 and T (the point of intersection of AB and CD) forming a triplet.

If moreover the points A, B, C, D, E and F lie on a conic, no other particularity appears than *the point U coinciding with K_1.* Of the three points of intersection K_1, L_1 and U of $K_1 L_1$ with the C_3 the points K_1 and U now coincide, *so that the C_3 touches the line $K_1 L_1$ in K_1.* In comparison with § 10 the particularity that appears is this that the point L_2 coincides with E whilst the pencil of rays L_2 has passed into the part improper of the envelope and the conic $ABCDEF$ into the part improper of the locus.

13. The case treated in the preceding paragraph is of course not the only one in which the series of points K and L are perspective, the condition of that perspectivity being single, the condition of the

coincidence of E and G being double. The condition of perspectivity can be found out of the condition that the point of intersection V of EF and GH (as point K) corresponds to itself (as point L). Now the conic $ABCD$ belonging to V (as point K) passes through the second point of intersection W of CV with the conic $ABEFC$, whilst C, W is a pair of points of the involution described on the conic $ABCDW$ by the pencil $ABEF$. If this pair of points also belongs to the involution described on that same conic by the pencil $CDGH$, the point L coincides evidently with V. So this is the case *when the conic of the pencil $CDGH$ touching the conic $ABCDW$ in C passes through W.* This condition for the perspectivity of the series of points K and L (where of course it must be possible to interchange C with D and likewise AB resp. EF with CD resp. GH) is evidently satisfied when E and G coincide.

If U is the centre of perspectivity, there exists between the rays of the pencil U and the conics of the pencil $ABCD$ a projective correspondence, where to the conics $ABCDE$, $ABCDF$, $ABCDG$, $ABCDH$, $ABCDW$ and $AB \,.\, CD$ correspond respectively the rays UE, UF, UG, UH, UV and $K_1 L_1$, whilst moreover to the conic $ABCDW$ all the rays of the pencil V correspond. So the C_5 of § 9 breaks up into the conic $ABCDW$, still belonging to the part proper of the locus, and a C_3 passing through the points $A, B, C, D, U, E, F, G, H, K_1$ and L_1, cutting the conic in A, B, C and D and the two points of intersection of UV with that conic.

The locus proper is thus a C_7 consisting of the lines AB and CD, the conic $ABCDW$ and the C_3 before mentioned. This C_7 has five double points differing from the base-points, namely, the triplet K_1, L_1, T and the pair formed by the points of intersection of UV with the conic $ABCDW$.

The C_3 is determined by the ten points, $A, B, C, D, E, F, G, H, K_1$ and L_1 so these ten points will have to lie on a C_3 if the above condition for the perspectivity is satisfied, and reversely it is easy to prove that when those ten points lie on a C_3 the series of points are perspective. Suppose namely that the series of points were not perspective. Then it would be possible by keeping the points A, B, C, D, E, F and G to construct on the line GH (thus by keeping the points K_1, L_1, V and W) by means of the former condition for perspectivity a point H' in such a manner that the series of points K and L are perspective; H' is then the second point of intersection of VG with the conic through C, D, G and W, touching the conic $ABCDW$ in C. So now the ten points A, B, C, D, E, F, G, K_1, L_1 and H' will lie on a C_3, however already determined by the

nine former points [1]) and thus the same as C_3 through the ten points $A, B, C, D, E, F, G, K_1, L_1$ and H. The line VG would then however have four points G, L_1, H and H' in common with this C_3.

So we arrive at the following simple result:

If the ten points $A, B, C, D, E, F, G, H, K_1$ and L_1 lie on the same cubic, the series of points K and L are perspective, whilst the centre of perspectivity coincides with the third point of intersection U of K_1L_1 with C_3. The envelope proper breaks up into the point U and the point of intersection V of EF and GH. The locus proper consists of the lines AB and CD, the cubic just mentioned and the conic through A, B, C, D and the two points, in which the right line UV intersects moreover the C_3 besides in U.

If E and G coincide, we immediately see that the above condition is satisfied. The point V lies then in point E so that one point of intersection of UV with C_3 differing from U becomes the point E; the indicated conic is thus the conic $ABCDE$, which now however belongs to the part improper of the locus.

14. *If G coincides with E and H with F*, then the series of points K and L are connective with double points in E and F. The pair of points PP' on an arbitrary conic of the pencil $ABCD$ is now continually described by the same line EF, thus belonging to the locus proper. If the conic passes through E or F the two involutions coincide, so that the conics $ABCDE$ and $ABCDF$ belong to the locus, but to the part improper of it. Moreover the lines AB and CD belong to the locus proper, *so that the latter consists of the three lines AB, CD and EF.* An envelope proper is no more at hand, the line connecting P and P' coinciding with AB, CD or EF when P and P' differ from the base-points.

In comparison with § 12 the particularity appears that U coincides with F, that the pencil of rays U passes into the part improper of the envelope and that the C_3 breaks up into the conic $ABCDF$ becoming improper and the right line EF.

The case of the pencils of conics $ABCD$, $ABEF$ and $CDEF$ can be profitably used to define with the help of the principle of the permanency of the number the order of the locus of P and P' and the class of the envelope of PP' for the case of pencils of conics lying arbitrarily with respect to each other. Starting from this simplest

[1]) The C_3 is only then not determined by these nine points if two of those points coincide in such a way that the connecting line is indefinite (e. g. G with E or K_1 with L_1). Then the ten points lie on a C_3, whilst it is easy to prove that the correspondence between K and L is perspective.

case, it is easy to reason that PP' coincides with AB, CD or EF and so the locus proper consists of these three lines and there is no envelope proper. The part improper of the locus however consists of six conics $ABCDE$, $ABCDF$, $ABEFC$, $ABEFD$, $CDEFA$ and $CDEFB$, the part improper of the envelope of the six points A, B, C, D, E and F. The total locus is thus of order fifteen, the total envelope of class six, so that for arbitrary position of the pencils of conics this same holds for the locus proper and the envelope proper.

Sneek, Nov. 1906.

Mathematics. — "*The locus of the pairs of common points of four pencils of surfaces.*" By Dr. F. Schuh. (Communicated by Prof. P. H. Schoute).

(Communicated in the meeting of December 29, 1906).

1. Given four pencils of surfaces (F_r), (F_s), (F_t) and (F_u) respectively of order r, s, t and u. The base-curves of those pencils can have common points or they can in part coincide, in consequence of which of three arbitrary surfaces of the pencils (F_s), (F_t) and (F_u) the number of points of intersection differing from the base-curves can become less than $s\,t\,u$; we call this number a, calling it b for the pencils (F_r), (F_t) and (F_u), c for the pencils (F_r) (F_s) and (F_u) and d for the pencils (F_r), (F_s) and (F_t). We now put the question:

What is the order of the surface formed by the pairs of points P and P', through which a surface of each of the four pencils is possible?

If the points P and P' do not lie on the base-curves we call the locus formed by those points the *locus proper* L on which of course still curves of points P may lie for which the corresponding point P' lies on one of the base-curves. If *one* triplet of pencils furnishes at least several points of intersection which are situated for all surfaces of those pencils on one of the base-curves, then there is a surface that *does* satisfy the question but in such a manner that if we assume P arbitrarily on this surface the point P' belonging to it is to be found on one of the base-curves; this surface we call the *part improper* of the locus, whilst both surfaces together are called the *total locus*.

2. To determine the order n of the locus proper L we find the points of intersection with an arbitrary right line l. On l we take

an arbitrary point Q_{stu} and we bring through that point surfaces F_s, F_t and F_u of the pencils (F_s), (F_t) and (F_u). Through each of the $a-1$ points of intersection of those surfaces not situated on the base-curves of those surfaces we bring a surface F_r. These $a-1$ surfaces F_r intersect the right line l together in $(a-1)r$ points Q_r, which we make to correspond to the point Q_{stu}. The coincidences of this correspondence are: 1st the points Q_{rstu} determining four surfaces which intersect one another once more in a point not lying on the base-curves, thus the n points of intersection with the surface L, 2nd the points of intersection with the surface R_{stu} belonging to the pencils (F_s), (F_t) and (F_u), the locus of the points S determining three surfaces whose tangential planes in S pass through one line.

To find the number of coincidences we have to determine the number of points Q_{stu} corresponding to an arbitrary point Q_r of l. To this end we take on l a point Q_{tu} arbitrarily and bring through it an F_t and an F_u. Through each of the b points of intersection of these surfaces with the surface F_r through Q_r (not lying on the base-curves) we bring an F_s, which b surfaces F_s intersect together the line l in bs points Q_s which we make to correspond to Q_{tu}. To find the number of points Q_{tu} corresponding to an arbitrary point Q_s of l we take Q_u arbitrarily on l, we bring through Q_s an F_s and through Q_u an F_u and through each of the c points of intersection of those surfaces with F_r an F_t, which furnish c surfaces F_t cutting l in ct points Q_t; reversely to Q_t belong du points Q_u, so that we find between the points Q_u and Q_t a (ct, du)-correspondence, of which the $ct+du$ coincidences give the points Q_{tu} belonging to the point Q_s. So between the points Q_{tu} and Q_s exists a $(bs, ct+du)$-correspondence, of which the coincidences consist of the r points of intersection of l with the surface F_r through Q_r and of the points Q_{stu} corresponding to Q_r; the number of these thus amounts to $bs+ct+du-r$.

So between the points Q_{stu} and Q_r there is an $(ar-r, bs+ct+du-r)$-correspondence with $ar+bs+ct+du-2r$ coincidences. To find out of this the number of points Q_{rstu} we must first determine the order of the surface R_{stu}.

This surface may be regarded as the surface of contact of the surfaces of the pencil (F_s) with the movable curves of intersections C_{tu} of the surfaces of the pencils (F_t) and (F_u) [1]. So the question is:

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[1]) We shall call this surface the surface of contact of the three pencils meaning by this that in a point of this "surface of contact" the surfaces of the pencils, though not touching one another, admit of a common tangent.

3. *To determine the order of the surface of contact of a twofold infinite system of twisted curves and a singly infinite system of surfaces.*

To this end we shall first suppose the two systems to be arbitrary.

To determine the order of the surface of contact we count its points of intersection with an arbitrary right line l. To this end we consider the envelope E_1 of the ∞^2 tangential planes of the curves of the system in their points of intersection with l and the envelope E_2 of the ∞^1 tangential planes of the surfaces of the system in their points of intersection with l.

The common tangential planes not passing through l of both envelopes indicate by means of their points of intersection with l the points of intersection of l with the surface of contact.

In order to find the class of the envelope E_1 (formed by the tangential planes of a regulus with l as directrix) we determine the class of the cone enveloped by the tangential planes passing through an arbitrary point Q of l. If the system of curves is such that φ curves pass through an arbitrary point and ψ curves touch a given plane in a point of a given right line, the tangential planes of E_1 through Q envelope the φ tangents in Q of the curves of the system through Q, and the line l counting ψ times; for each plane through l is to be regarded ψ times as tangential plane, there being ψ curves of the system cutting l and having a tangent situated in this plane. *The envelope E_1 is thus of class $\varphi + \psi$ and has l as ψ-fold line*[1]).

To find the class of the envelope E_2 we determine the number of its tangential planes through an arbitrary point Q of l. If now the system has μ surfaces through a given point and ν surfaces touching a given right line, the tangential planes of the envelope passing through Q are the tangential planes in Q to the μ surfaces passing through Q and the tangential planes of the ν surfaces touching l. *So the envelope E_2 is of class $\mu + \nu$ with ν tangential planes through l.*

Hence both envelopes have $(\varphi + \psi)(\mu + \nu)$ common tangential planes. Each of the ν tangential planes of E_2 passing through l is however a ψ-fold tangential plane of E_1 and so it counts for ψ common tangential planes. So for the number of common tangential planes not passing through l, thus the number of points of intersection of l with the surface of contact we find:

$$(\varphi + \psi)(\mu + \nu) - \psi\nu = \varphi\nu + \psi\mu + \varphi\mu ,$$

therefore:

[1]) The regulus as locus of points has however line l as φ-fold line.

The surface of contact of a system (φ, ψ) *of* ∞^2 *twisted curves* [1]) *and a system* (μ, ν) *of* ∞^1 *surfaces* [2]) *is of order* $\varphi\nu + \psi\mu + \varphi\mu$ [3]).

4. To determine the order of the surface of contact [4]) of the systems $\mu_1, \nu_1)$, (μ_2, ν_2) and (μ_3, ν_3) each of ∞^1 surfaces, we regard the system (φ, ψ) of the curves of intersection of the systems (μ_1, ν_1) and (μ_2, ν_2). Of these curves of intersection $\mu_1\mu_2$ pass through a given point, so $\varphi = \mu_1\mu_2$. The ψ points, where the curves of intersection touch a given plane in a point of a given right line, are the points of intersection of that given line with the curve of contact of the systems (μ_1, ν_1) [5]) and (μ_2, ν_2) of plane curves, according to which the given plane intersects the systems of surfaces (μ_1, ν_1) and (μ_2, ν_2). This curve of contact is of order $\mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2$, thus:

$$\psi = \mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2.$$

The surface of contact to be found is thus the surface of contact of a system $(\mu_1\mu_2, \mu_1\nu_2 + \mu_2\nu_1 + \mu_1\mu_2)$ of ∞^2 twisted curves and a system (μ_3, ν_3) of ∞^1 surfaces, so that we find:

The surface of contact of three systems (μ_1, ν_1), (μ_2, ν_2) *and* (μ_3, ν_3) *of* ∞^1 *surfaces is of order*

$$\mu_2\mu_3\nu_1 + \mu_3\mu_1\nu_2 + \mu_1\mu_2\nu_3 + 2\mu_1\mu_2\mu_3.$$

If the three systems are the pencils (F_s), (F_t) and (F_u) we have

$$\mu_1 = \mu_2 = \mu_3 = 1,$$

$$\nu_1 = 2(s-1) \quad , \quad \nu_2 = 2(t-1) \quad , \quad \nu_3 = 2(u-1).$$

So we find:

The surface of contact F_{stu} *of the three pencils of surfaces* (F_s), (F_t) *and* (F_u) *is of order*

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[1]) System with φ curves through a given point and ψ curves cutting a given line and touching in the point of intersection a given plane through that line.

[2]) System with μ surfaces through a given point and ν surfaces touching a given right line.

[3]) This result is also immediately deducible from the SCHUBERT formula

$$xp^2 = p'^3 \,.\, G + p'g'_e \,.\, p^2g_e + p'^3 \,.\, p^2g_e$$

(Kalkül der abzählenden Geometrie, formula 13, page 292) for the number of common elements with a point lying on a given line of a system Σ' of ∞^3 and a system Σ of ∞^4 right lines with a point on it. If we take for Σ' the tangents with point of contact of the system of curves (φ, ψ) and for Σ the tangents with point of contact of the system of surfaces (μ, ν), then

$$p'^3 = \varphi \quad , \quad p'g'_e = \psi \quad , \quad G = \nu \quad , \quad p^2g_e = \mu,$$

whilst xp^2 is the order of the surface of contact.

[4]) Locus of the points, where the surfaces of the three systems have a common tangent.

[5]) System of ∞^1 curves of which μ_1 pass through a given point and ν_1 touch a given right line.

$$2\,(s + t + u - 2).$$

5. To return to the question which gave rise to the preceding considerations we find for the number of points Q_{rstu} on the arbitrary line l, which are the points of intersection of l with the locus proper L:

$$ar + bs + ct + du - 2r - 2\,(s + t + u - 2) =$$
$$= ar + bs + ct + du - 2\,(r + s + t + u) + 4.$$

So we find:

The locus L of the pairs consisting of two movable points common to a surface out of each of the pencils (F_r), (F_s), (F_t) and (F_u) of orders r, s, t and u, and not lying on the base-curves, is a surface of order

$$ar + bs + ct + du - 2\,(r + s + t + u) + 4.$$

Here a is the number of points of intersection not necessarily situated on the base-curves of the pencils (F_s), (F_t) and (F_u); b the analogous number for the pencils (F_r), (F_t) and (F_u), etc.

6. It the pencils have an arbitrary situation with respect to each other, then $a = stu$, etc., so that then the order of the locus becomes

$$4\,(rstu + 1) - 2\,(r + s + t + u).$$

That order is lowered when three of the base-curves have a common point or two of the base-curves have a common part, which lowering of the order can be explained by separation as long as the total locus is definite, i. e. as long as the four base-curves have no common point and no triplet of base-curves have a common part. For, if A_{rstu} is a common point of four base-curves then the surfaces of the four pencils passing through an entirely arbitrary point P have another second point in common, namely A_{rstu}; if B_{stu} is a curve forming part of the base-curves B_s, B_t and B_u of the pencils (F_s), (F_t) and (F_u), then the surfaces of the pencils passing through an arbitrary point P have moreover the points of intersection in common of B_{stu} with the surface F_r through P; so in both cases the arbitrary point P belongs to the total locus.

If the basecurves B_s, B_t and B_u have a common point A_{stu} then on account of that point the number a is diminished by unity without having any influence on b, c and d. The order of L is thus lowered by r on account of it, which is immediately explained by the fact that *the surface F_r passing through A_{stu} separates itself from the locus.*

If the base-curves B_t and B_u have a curve B_{tu} in common of which for convenience we suppose that it does not intersect the base-curves B_r and B_s, this B_{tu} has no influence on c and d, whilst a is lowered with sm and b with rm, where m represents the order of the curve B_{tu}; for, when F_s, F_t and F_u are three arbitrary surfaces always sm points of intersection lie on B_{tu}. The order of L is thus lowered with $2rsm$ by B_{tu}. This can be explained by the fact, that *the locus of the curves of intersection C_{rs} of surfaces F_r and F_s passing through a selfsame point of B_{tu}* [1]) *separates itself from the locus of P and P'*. That the locus of those curves of intersection is really of order $2rsm$ is easily evident from the points of intersection with an arbitrary line l. We can bring through an arbitrary point Q_r of l an F_r cutting B_{tu} in rm points; through each of those points of intersection we bring an F_s, which rm surfaces F_s cut the right line l in rsm points Q_s. To Q_r correspond rsm points Q_s and reversely. The $2rsm$ coincidences are the points of intersection of l with the locus of the curves of intersection C_{rs}.

7. The base-curves B_r, B_s, B_t and B_u of the pencils are morefold curves of the surface L. If A_r is a point of B_r but not of the other base-curves, then A_r is an $(a-1)$-fold point of L. For, the surfaces F_s, F_t and F_u through A_r intersect one another in $a-1$ points, not lying on the base-curves, each of which points furnishes together with A_r a pair of points satisfying the question. Each point of B_r is thus an $(a-1)$-fold point, i. o. w. *B_r is $(a-1)$-fold curve of the surface L.*

Let A_{rs} be a point of intersection of the base-curves B_r and B_s, but not a point of B_t and B_u. An arbitrary point P of the curve of intersection C_{tu} of the surfaces F_t and F_u through A_{rs} furnishes now together with A_{rs} a pair of points PP' satisfying the question properly, as A_{rs} is for each triplet of pencils a movable point of intersection not lying on the base-curves. If we let P describe the curve C_{tu}, then the tangent l_{rs} in A_{rs} to the curve of intersection of the surfaces F_r and F_s through P describes the cone of contact of L in the conic point A_{rs}. The tangents m_r and m_s in A_{rs} to B_r and B_s are $(a-1)$- resp. $(b-1)$-fold edges of the cone. This cone is cut by the plane through m_r and m_s only according to the line m_r counting $(a-1)$-times and the line m_s counting $(b-1)$-times, as another line l_{rs} lying in this plane would determine two surfaces

[1]) If B_{tu} cuts the curve B_s in a point A_{stu}, then the surface F_r passing through A_{stu} separates itself from the locus of the curves of intersection C_{rs}.

F_r and F_s touching each other in A_{rs}, whose curve of intersection, however, does not cut the curve C_{tu}. *The tangential cone of L in A_{rs} is thus of order $a+b-2$* [1]).

Let $A_{rs}^{(1)}$ be a point of a common part B_{rs} of the base-curves B_r and B_s but not a point of B_t and B_u. We get a pair of points PP' with a point P' coinciding with $A_{rs}^{(1)}$ when the surfaces F_r and F_s have in $A_{rs}^{(1)}$ a common tangential plane V_{rs} and pass through a selfsame point P of the curve of intersection C_{tu} of the surfaces F_t and F_u through $A_{rs}^{(1)}$. If we let P describe the curve C_{tu}, then on account of that between the planes V_r and V_s, touching in $A_{rs}^{(1)}$ the surfaces F_r and F_s through P, a correspondence is arranged, where to V_r correspond $b-1$ planes V_s and to V_s correspond $a-1$ planes V_r. One of the $a+b-2$ planes of coincidences is the plane through the tangents in $A_{rs}^{(1)}$ to B_{rs} and C_{tu}; this plane furnishes no plane V_{rs}. The remaining $a+b-3$ planes of coincidence are planes V_{rs} and indicate the tangential planes in $A_{rs}^{(1)}$ to the surface L. *So B_{rs} is an $(a+b-3)$-fold curve of L.*

8. Let us then consider a common point A_{rst} of the base-curves B_r, B_s and B_t. We get a pair of points PP' with a point P' coinciding with A_{rst}, when the tangential planes in A_{rst} to F_r, F_s and F_t pass through one line l_{rst} and these surfaces intersect one another again in a point P of the surface F_u passing through A_{rst}. There are ∞^1 such lines l_{rst}, forming the tangential cone of L in point A_{rst}. The tangents m_r, m_s and m_t in A_{rst} to B_r, B_s and B_t are $(a-1)$-, $(b-1)$- and $(c-1)$-fold edges of that cone. So the plane through m_r and m_s furnishes $a+b-2$ lines of intersection with the cone coinciding with m_r and m_s. Moreover $c-2$ other lines l_{rst} lie in this plane. For, the surfaces F_r and F_s touching this plane intersect F_u in $c-2$ points not lying on the base-curves; the surfaces F_t through those points intersect the plane through m_r and m_s according to curves whose tangents in A_{rst} are the mentioned

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[1]) The order of this cone can also be found out of the number of lines of intersection with an arbitrary plane ε through A_{rs}. If l_r and l_s are the lines of intersection of ε with the tangential planes in A_{rs} to the surfaces F_r and F_s through P, then to l_r correspond $b-1$ lines l_s and to l_s correspond $a-1$ lines l_r, so that in the plane ε lie $a+b-2$ lines l_{rs}.

lines l_{rst}. *So the tangential cone of* L *in* A_{rst} *is of order* $a+b+c-4$ [1]).

A point of intersection $A^{(1)}_{rst}$ of B_r with a common part B_{st} of the base-curves B_s and B_t is a conic point of L, the tangential cone of which is formed as in the previous case by ∞^1 lines l_{rst}. The tangents m_r and m_{st} in $A^{(1)}_{rst}$ to B_r and B_{st} are $(a-1)$ and $(b+c-3)$-fold edges of that cone. As no other lines l_{rst} lie in the plane through m_r and m_{st}, it is evident *that the tangential cone of* L in $A^{(1)}_{rst}$ *is likewise of order* $a+b+c-4$ [1]).

Let $A^{(2)}_{rst}$ be a point of a common part B_{rst} of the base-curves B_r, B_s and B_t. The point P' of the pair of points PP' coincides with $A^{(2)}_{rst}$ when the surfaces F_r, F_s and F_t have in $A^{(2)}_{rst}$ the same tangential plane V_{rst} and cut one another in another point P of the surface F_u through $A^{(2)}_{rst}$. If we now consider an F_r and an F_s having in $A^{(2)}_{rst}$ the same tangential plane V_{rs} and if we consider through each of the $c-1$ points of intersection of F_r, F_s and F_u not lying on the base-curves an F_t of which we indicate the tangential plane in $A^{(2)}_{rst}$ by V_t then to V_{rs} correspond $c-1$ planes V_t and to V_t correspond $a+b-1$ planes V_{rs} (as for given V_t a (b, a)-correspondence exists between V_r and V_s of which V_t is one of the planes of coincidence). Among the $a+b+c-2$ planes of coincidence V_{rs} V_t there are however *three* which give no plane V_{rst}, namely the planes V_{rs}, for which the corresponding surfaces F_r and F_s furnish with F_u three points of intersection coinciding with $A^{(2)}_{rst}$. For this is necessary that F_u touches in $A^{(2)}_{rst}$ the movable intersection of F_r and F_s. Now the tangents of those intersections for all surfaces F_r and F_s touching each other in $A^{(2)}_{rst}$ form a cubic cone having for double edge the tangent m_{rst} to B_{rst} in point $A^{(2)}_{rst}$ [2]). This cone is cut by the tangential plane in $A^{(2)}_{rst}$ to F_u according to three lines, furnishing with m_{rst} planes V_{rs} which are planes of coincidence

[1]) This order can also be determined out of the number of lines l_{rst} in a plane ε passing through A_{rst}. In this plane we find a $(c-1,\ a+b-2)$-correspondence between lines l_s and lines l_r of which however the line of intersection of ε with the tangential plane in A_{rst} to F_u is a line of coincidence, but no line l_{rst}.

[2]) This is immediately evident if we take for (F_r) a pencil of planes and for (F_s) a pencil of quadratic surfaces all passing through the axis B_r of the pencil of planes. The cone under consideration then becomes the cone of the generatrices of the quadratic surfaces passing through a given point of B_r. We can easily convince ourselves that the same result holds for arbitrary pencils of surfaces.

of V_{rs} and V_t, but not planes V_{rst}. So there are $a+b+c-5$ planes V_{rst}, which are the tangential planes of L in the point $A^{(2)}_{rst}$, i. o. w. B_{rst} *is* $(a+b+c-5)$*-fold curve of surface* L.

9. We then consider a common point A_{rstu} of the four base-curves. We get a pair of points PP' with point P'' coinciding with A_{rstu} when F_r, F_s, F_t and F_u have in A_{rstu} a common tangent l_{rstu} and all pass once again through a selfsame point P. The ∞^1 lines l_{rstu} form the tangential cone of L in A_{rstu}. To determine the number of lines l_{rstu} in an arbitrary plane ε through A_{rstu} we take in this plane an arbitrary line l_{rst} through A_{rstu} and we bring through the $d-1$ points of intersection (not lying on the base-curves) of the surfaces F_r, F_s and F_t touching l_{rst} the surfaces F_u, whose tangential planes in A_{rstu} cut the plane ε according to lines, which we shall call l_u. To l_{rst} now correspond $d-1$ lines l_u and to l_u correspond $a+b+c-2$ lines l_{rst}, as there exists between l_{rs} and l_t when l_u is given a $(c, a+b)$-correspondence, of which l_u and the line of intersection of ε with the plane through the tangents in A_{rstu} to B_r and B_s are lines of coincidence, but not lines l_{rst}. So there are $a+b+c+d-3$ lines of coincidence l_{rst} l_u of which however *three* are not lines l_{rstu}. The common tangents in A_{rstu} of the surfaces F_r, F_s and F_t possessing three points of intersection coinciding with A_{rstu} and where therefore the intersection of two of those surfaces shows a contact of order two to the third, form namely a cubic cone [1]) of which the lines of intersection with ε are lines of coincidence but not lines l_{rstu}. So in ε lie $a+b+c+d-6$ lines l_{rstu}, i. o. w. *the tangential cone of* L *in* A_{rstu} *is of order* $a+b+c+d-6$ [2]).

[1]) This is again evident when taking for (F_r) and (F_s) pencils of planes with coplanar axes B_r and B_s and for (F_t) a pencil of quadratic surfaces passing through a line containing the point of intersection S of B_r and B_s. The line of intersection of the planes F_r and F_s shows only then a contact of order two to F_t when that line of intersection lies entirely on F_t, so that the cone under consideration becomes again the cone of the generatrices of the quadratic surfaces passing through S.

[2]) That order can also be found out of the lines of intersection with the plane V_{rs} through the tangents m_r and m in A_{rstu} to B_r and B_s. Those lines of intersection are: the line m_r, counting $(a-1)$-times, the line m_s counting $(b-1)$-times and $c+d-4$ other lines. This last amount we find by drawing in plane V_{rs} an arbitrary line l_t through A_{rstu}. The surface F_t touching l_t cuts the surfaces F_r and F_s touching V_{rs} in $d-1$ points (not lying on the base-curves) through which points we bring surfaces F_u whose tangential planes in A_{rstu} cut the plane V_{rs} according to lines to be called l_u. Between the lines l_t and l_u we now have a $(d-1, c-1)$-correspondence of which the nodal tangents in A_{rstu} of the intersection of the surfaces F_r and F_s touching V_{rs} are lines of coincidence. The remaining $c+d-4$ lines of coincidence are lines l_{rstu}.

The preceding considerations hold invariably for a point $A^{(1)}_{rstu}$ lying on the base-curves B_r and B_s and the common part B_{tu} of the base-curves B_t and B_u [1]).

In a point of intersection $A^{(2)}_{rstu}$ of B_{rs} and B_{tu} the tangential cone is likewise of order $a+b+c+d-6$ as that cone has the tangents m_{rs} and m_{tu} to B_{rs} and B_{tu} as $(a+b-3)$ and $(c+d-3)$ fold edges, whilst in the plane through m_{rs} and m_{tu} no other right lines l_{rstu} are lying.

A point of intersection $A^{(3)}_{rstu}$ of B_r and B_{stu} is also a $(a+b+c+d-6)$ fold point of L as m_r and m_{stu} are $(a-1)$- and $(b+c+d-5)$-fold edges of the tangential cone and the only lines of intersection of that cone with the plane through m_r and m_{stu}.

If finally $A^{(4)}_{rstu}$ is a point of a common part B_{rstu} of the four base-curves, then the point P' of the pair of points PP' coincides with $A^{(4)}_{rstu}$ when the surfaces F_r, F_s, F_t and F_u have in A^{4}_{rstu} the same tangential plane V_{rstu} and all pass through a same point P. Let us now assume an arbitrary plane V_{rst} passing through the tangent m_{rstu} in $A^{(4)}_{rstu}$ to B_{rstu}. The surfaces F_r, F_s and F_t touching this plane in $A^{(4)}_{rstu}$ cut one another in $d-1$ points P, through which we bring surfaces F_u, of which we call the tangential planes in $A^{(4)}_{rstu}$ V_u. Thus we obtain a correspondence, where to V_{rst} correspond $d-1$ planes V_u and reversely to V_u correspond $a+b+c-1$ planes V_{rst}; for when V_u is given there is between V_{rs} and V_t a $(c, a+b)$ correspondence, of which V_u is plane of coincidence, but not a plane V_{rst}. So there are $a+b+c+d-2$ planes of coincidence $V_{rst}V_u$, of which however *five* are not planes V_{rstu}. These are namely the tangential planes of the surfaces F_r, F_s and F_t of which one more point of intersection coincides with $A^{(4)}_{rstu}$ which

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[1]) It is also easy to see from the lines of intersection with the plane V_{stu} through the tangents m_s and m_{tu} to B_s and B_{tu} that the tangential cone in $A^{(1)}_{rstu}$ is of order $a+b+c+d-6$. The line m_s counts for $b-1$ lines of intersection, the line m_{tu} for $c+d-3$. Further, the surfaces F_s, F_t and F_u touching V_{stu} cut one another in $a-2$ points not lying on the base-curves; through those points we bring surfaces F_r, whose tangential planes in $A^{(1)}_{rstu}$ cut the plane V_{stu} along to lines which lie on the tangential cone.

occurs five times [1]). So there remain $a+b+c+d-7$ planes V_{rstu} which are the tangential planes of L in the point $A^{(4)}_{rstu}$, so that B_{rstu} is a $(a+b+c+d-7)$ fold curve of L.

10. So we find:

Of the locus proper L of the pairs of points P and P' the base-curve B_r of the pencil (F_r) is $(a-1)$-fold curve, the common part B_{rs} of the base-curves B_r and B_s is $(a+b-3)$-fold curve, the common part B_{rst} of the base-curves B_r, B_s and B_t is $(a+b+c-5)$ fold curve and the common part B_{rstu} of the four base-curves is $(a+b+c+d-7)$-fold curve. The points of intersection of the base-curves are conic points of L, namely a point of intersection of B_r and B_s is $(a+b-2)$-fold point, a point of intersection of B_r, B_s and B_t or of B_r and B_{st} is $(a+b+c-4)$-fold point and a point of intersection of B_r, B_s, B_t and B_u or of B_r, B_s and B_{tu} or of B_{rs} and B_{tu} or of B_r and B_{stu} is $(a+b+c+d-6)$-fold point. [2])

11. The base-curves of the pencils are not the only singular curves of the surface L. There are namely ∞^1 triplets of points lying on a surface of each of the pencils. These triplets of points form a double curve of L. If P, P', P'' is such a triplet and if $P1$ and $P2$ are the sheets through P of the surface, then the sheets $P'1$ and $P''2$ correspond to them. Through P' passes another sheet $P'3$ and through P'' a sheet $P''3$ which sheets correspond mutually. The pair of points not lying on the base-curves is movable along the sheets $P1$, $P'1$, along the sheets $P2$, $P''2$ and along the sheets $P'3$, $P''3$; on the base-curve a third point then joins the pair.

Further there is still a finite number of quadruples of points,

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[1]) The number *five* is found in the following way. The tangents of the movable intersections of surfaces F_s and F_t touching each other in $A^{(4)}_{rstu}$ form a cubic cone having the tangent m_{rstu} to B_{rstu} as double line. Such an intersection shows to the surface F_r a contact of order two when it touches the movable intersection of F_r and F_t, so if its tangent in $A^{(4)}_{rstu}$ lies on the cubic cone belonging to the pencils (F_r) and (F_t). As this last cone has also m_{rstu} as double edge, both cones have $9-4=5$ lines of intersection differing from m_{rstu} which connected with m_{rstu} furnish the five planes under consideration.

[2]) If the total locus is not indefinite, i. o. w. if there is no point common to the four base-curves then B_r is a $(stu-1)$-fold curve and B_{rs} a $(stu+rtu-2)$ fold curve of the total locus whilst a point of intersection of B_r and B_s is a $(stu+rtu-2)$-fold point and a point of intersection of B_r, B_s and B_t or of B_r and B_{st} a $(stu+rtu+rsu-3)$-fold point of it.

through which passes a surface out of each of the pencils. Through the points P, P', P'' and P''' of such a quadruple pass three sheets of the surface L and three branches of the double curve. The 12 branches of the double curve through those four points we can call $P1, P2, P3, P'1, P'2, P'4, P''1, P''3, P''4, P'''2, P'''3, P'''4$, in such a way that the triplet of points is movable along the branches $P1, P'1, P''1$, along $P2, P'2, P'''2$, along $P3, P''3, P'''3$ and along $P'4, P''4, P'''4$. If the sheet of L passing through $P1$ and $P2$ is called $P12$, then the corresponding sheets (i. e. sheets along which the pair of points not lying on the double curve is movable) are $P12$ and $P'12$, $P13$ and $P''13$, etc.

Geophysics. — "*Current-measurements at various depths in the North Sea.*" (First communication). By Prof. C. H. WIND, Lt[t]. A. F. H. DALHUISEN and Dr. W. E. RINGER.

In the year 1904 accurate measurements of the currents in the North Sea [1]) were started by the naval lieutenant A. M. VAN ROOSENDAAL, at the time detached to the "Rijksinstituut voor het Onderzoek der Zee", having been proposed and guided by the Dutch delegates to the International Council for the Study of the Sea.

By him four apparatus were put to the test, viz. 2 specimens of the current-meter of PETTERSSON [2]), one of that of NANSEN [3]) and one of that of EKMAN [4]), all destined to determine the direction and the velocity of the current at every depth.

The experiments were partly made on the light-ship "Haaks", where Dr. J. P. VAN DER STOK, the Marine Superintendent of the Kon. Nederl. Meteorologisch Instituut, also took part in them. Other experiments were made in the harbour of Nieuwediep and further, from the research-steamer "Wodan", in the open North Sea at a station (H2) of the Dutch seasonal cruises [5]), situated at Lat. 53°44′ N. and Long. 4°28′ E.

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[1]) Cons. Perm. Intern. p. l'expl. de la mer, Publications de circonstance No. 26 : A. M. VAN ROOSENDAAL und C. H. WIND, Prüfung von Strommessern und Strommessungsversuche in der Nordsee. Copenhague, 1905.

[2]) Publ. de circ. No. 25.

[3]) „ „ „ No. 34.

[4]) „ „ „ No. 24.

[5]) Quarterly cruises of the countries taking part in the international study of the sea, along fixed routes, observations being made at definite points or "stations".

The apparatus of NANSEN appeared to be unfit for the measurements on the North Sea; it was not calculated for the strong tidal currents occurring there (e.g. 60—100 cm/sec.), and also the putting out of the apparatus in unfavourable weather was hardly possible without doing harm to the instrument. In more quiet water, however, it seems to be very useful.

The apparatuses of PETTERSSON and EKMAN appeared to be better fit for the observations in the North Sea. Some improvements in the construction were proposed, partly also put into practice, by VAN ROOSENDAAL and WIND, by which the instruments have gained in fitness. For a description of the construction of the current-meters used, and the experience made in using them, we may refer to the publications mentioned. The following few words may be sufficient here.

It appeared that pretty large oscillations, e. g. 15° to both sides round the longitudinal axis, did not yet render observation impossible. In 32 out of nearly 200 observations by VAN ROOSENDAAL as much as the figure 4 was noted for the motion of the sea, in 40 to 50 cases the oscillations amounted to 10 à 20° to either side, and yet the accuracy and certainty of these measurements were only exceptionally insufficient.

In the parallel-observations with the apparatus of PETTERSSON and EKMAN the agreement in indicating the *velocity* appeared satisfactory. In one series of 23 measurements e. g. the average difference amounted to 4.8 cm/sec, whilst the smallest was 3.1, the greatest 6.3.

Nor did the indications of *direction*, as given by the two instruments, show great differences. The observations with EKMAN's apparatus bear to some extent a check in themselves, as, by the construction of the instrument, every observation includes a series of consecutive readings at small intervals. In by far the greater part of the readings-observations these separate did not considerably vary. In 128 cases the direction of the current could be estimated from them:

To less than 10°	in 105 cases,
10—20	15
20—30	2
30—40	0
40—50	2
more than 50°	4.

Compared with the probable direction, as derived from the instrument of EKMAN, that which was determined by means of PETTERSON's instrument deviated:

in 65	cases less than 10
37	10—20
15	20—30
5	30—40
1	40—50
8	more than 50°.

VAN ROOSENDAAL and WIND took from the whole of observations made at station H_2 the most probable values direction and velocity of current at the various depths and represented them graphically. They constructed for the different series of observations, each lasting 12 or 24 hours, in the first place *central vector-diagrams*, by drawing from a fixed point the successively determined currents as radii-vectores and connecting the terminal points by means of straight lines or of a curve, and in the second place *progressive vector-diagrams*, by drawing the current-vectors, this time interpolated for the successive full hours, one after and attached to the other. In the first kind of diagrams the periodical currents, and in the second the residual currents make themselves most apparent.

The measurements were continued at the station H2 during all the following seasonal cruises of the "Rijksinstituut", first by VAN ROOSENDAAL and afterwards by the naval lieutenant DALHUISEN, who succeeded the former in his detachment. At the more recent measurements the current-meter of EKMAN was always made use of.

The following table gives the dates of the series of observations and the number of measurements [1]).

N°.	Time.	Number of Measurements.	Depth (M.)	Apparatus.	Observer.
1.	from 16 Aug. '05 4.12 p.m. till 17 „ „ 4.54 »	56	5,20,35	EKMAN.	VAN ROOSENDAAL.
2.	from 7 Nov. '05 7.48 a.m. till 8 „ „ 12.34 p.m.	53	» » »	»	VAN ROOSENDAAL and DALHUISEN
3.	from 7 Febr. '06 7.20 p.m. till 8 „ „ 5.53 a.m.	18	» » »	»	DALHUISEN.
4.	from 2 May '06 6.35 a.m. till 3 „ „ 6.41 »	54	» » »	»	»

[1]) A more detailed description of these observations forms the contents of the last issue of the "Publications de circonstance" No. 36.

At these researches wind and weather were on the whole favourable; the wind was in a few cases noted 7 at most, at which force, however, the observations had to be put a stop to in February 1906 [1]).

On the plate added, the new measurements are again represented graphically in central and progressive vector-diagrams. Also the central diagrams, have been constructed this time with the aid of values interpolated for full hours, the directly measured values however, having still been indicated by dots.

It is principally to give a full idea of the variability in direction and velocity of the currents, that these diagrams of the new series of observations have been reproduced fully here.

Comparing the values of the velocity near the surface and in the depth, we see that in 3 out of the 4 cases they show a rather distinct decrease at an increase of depth. Also at the former series of observations at H2 (3—4 Aug., 8—9 Aug. and 2—3 Nov. 1905 [2]), also 8—9 Febr. 1905 [3])) the same result was arrived at.

Also differences of phase in the periodical currents are noticed in most cases between the surface and the depth, though a distinct law may not immediately be obvious here.

The striking difference in amplitude of the tidal currents during the observations in August 1905 and February 1906 on the one side and that of November 1905 and May 1906 on the other, is certainly connected with the age of the tide, as it was with the first nearly spring-tide ($15^1/_2$ and 14 days after N. M.), with the last nearer to dead neap (10 and 0 days after N.M.).

The small number of series of observations that can be disposed of, does of course not allow at all to already think of a calculation of tidal constants, nor to give a correct description of the average variation of the currents. The unmistakable general agreement, however, between the different current-diagrams justifies sufficiently an attempt to compose them. As no doubt moon-tide will have played

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[1]) The reliability of the new observations is no doubt greater than that of the former, if we take into consideration, that in August and November 1905 and in February and May 1906 the Wodan lay moored, so that her motion was considerably smaller than on the former occasions, when she had cast only one anchor. It may still be mentioned that an experimental and theoretical investigation was started about the influence of the movements of the ship upon the indications of the current-meter, which, however, has not yet led to a satisfactory result.

[2]) Publ. de Circ. N°. 26.

[3]) „ „ „ N°. 36.

the principal part, we have thought best for this purpose to compose for the successive full moon-hours the current-values as they follow by interpolation from the different diagrams. The averages thus obtained have been combined in new diagrams, which are represented on the plate, in the last column of figures, and that by black curved lines.

In order to complete the matter and to allow comparisons, in the same way average diagrams have been derived from the observations made in the past year at H2 (see above) and represented in the same figures on the plate by black-and-white curves.

The arrows drawn in these figures indicate: in the central diagrams the direction of the current at the moon's transit, in the progressive diagrams the total residual current during a half moon-day.

A comparison of the average current-diagrams for various depths or also of the newer with the older ones might give rise to all kinds of remarks. With a view to the small number of data, however, on which the diagrams are based, it would perhaps be inconsiderate to mention all of them here. We therefore confine ourselves to what follows.

Difference in Phase of the tide at different depths.

	August 1905—May 1906		August—November 1904	
	20 M.—5 M.	35 M.—20 M.	20 M—70 M.	30 M.—20 M.
☾ Transit	18°	5°	0	3°
one hour after »	24	— 6	—13	14
2	23	— 3	— 8	5
3	20	5	— 3	6
4	25	— 2	5	14
5	26	0	18	— 5
6	25	8	3	22
5 » before »	19	17	0	17
4	25	15	— 9	17
3	8	— 6	— 3	25
2	4	10	— 6	24
1	6	11	— 6	11
Average	13°85′	4°30′	—1°50′	12°45

The tidal curve shows not only at different depths, but also in the older and newer observations, generally the same *shape*. Its *size*, on the other hand, both in the older and more recent observations, appears to be smaller near the bottom than near the surface. Also its *orientation* and the situation of the point in it, which relates to the moment of the moon's transit, or, more generally, the *phase* of the tidal current, seems to change in a definite sense as the depth increases. This last relation may be specially illustrated by the following table.

It appears from the table, that the tide is on the whole accelerated in the depth, compared with higher layers; but the table also proves that the phenomenon underlies varying influences, besides constant causes, among which perhaps may be reckonned the shape of the bottom of the sea and the rotation of the earth.

The residual current is by no means constant; at the new observations it has been much stronger than at the old; it shows considerable fluctuations also, when the progressive diagrams of the different days of observation are compared. At the new observations this residual current was on an average stronger near the surface than in deeper layers. This particular may perhaps be principally attributed to the action of persisting winds, which at least on the observations of August 1905 and May 1906 had a very marked influence, rendered quite obvious by the special diagrams for these dates.

The figures for the residual current as deduced from the newer observations are the following:

Depth.	Direction.	Velocity.
5 M	N 304° E	1/4 mile p. hour
20	317	1/8
35	309°	1/9 ,

as deduced from the older:

7 [1]) M.	N 319° E	1/19 mile p. hour
20	295°	1/26
30	323°	1/18 .

These results are worth comparing with the following table of values for the year-average of the residual current at the Noord-Hinder (Lat. 51°35'.5 N., Long. 2°37' E.), calculated by VAN DER STOK [2]) from current-estimations near the surface during five consecutive years.

[1]) Average of depths of 1, 4, 5, 6, 10 M.; at a depth of 35 M. measurements were made by VAN ROOSENDAAL only in February 1905.

[2]) J. P. VAN DER STOK, Etudes des Phénomènes de Marée sur les côtes néerlandaises; Kon. Ned. Met. Inst. No. 90, II. p. 67, 1905.

Year.	Direction.	Velocity.
1890	N 16° E	0.024 miles p. hour.
91	15	62
92	16	35
93	29	47
94	27	47
Average	N 21° E	0.044 miles p. hour.

Here it appears that the average residual current, which — as we mention in passing — has at this point quite another direction than at H2, even from year to year does not at all remain constant in strength which may perhaps be an indication for differences in the quantity of Atlantic water, entering through the English Channel from year to year.

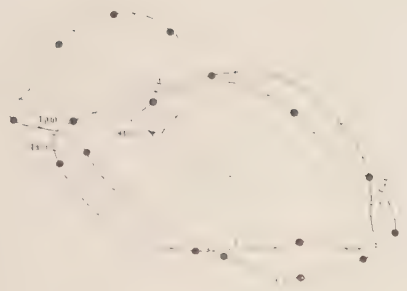
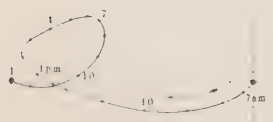
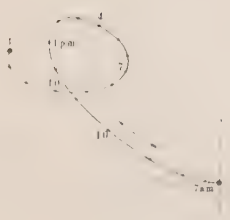
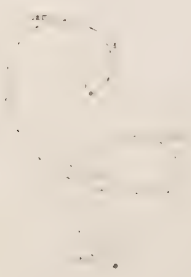
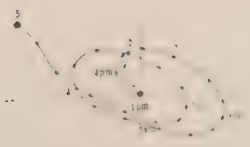
The question may be put, whether and how far the results attained by the current-measurements described, deviate from what is known from the charts, in general use, about the currents near the station H2, The subjoined table allows of a comparison with statements, borrowed from a chart, published by the British Admiralty [1]), and shows

Hour.	From the Charts.		Observed.	
	Direction.	Velocity (m. p. h.).	Direction.	Velocity (m. p. h.).
5 before H.W.Dover	N 90° E	0,3—0 2	N 73° E	0,3
4	110	0,5—0,3	115	0,4
3	135	0,9—0,6	147	0,4
2	160	0,6—0 4	189	0,3
1	180	0,3—0.2	227	0.4
H. W. Dover	—	0	266	0,5
1 after H.W. Dover	260	0 2—0,2	280	0 5
2	300	0,6—0,4	296	0,6
3	300	1,0—0,7	331	0 5
4	315	0,6—0,4	342	0,4
5	0	0,3—0,2	9	0,4
6	50	—	40	0,4

[1]) Tidal Streams North Sea 1899.

CURRENTS OBSERVED at H, (Lat. 53°44′, Long. 4°28′).

(True direction.)

	1905, August 16—17.	1905, November 7—8.	1906, Februar 7—8.	1906, May 2—3.	Averages (at figures indicate moon-hours).
	CENTRAL DIAGRAMS.				
	0 10 20 30 40 50 cm. p. sec.. 0 ½ 1 1½ 2 miles p. hour.				
5 M.					
20 M.					
35 M.					
	PROGRESSIVE DIAGRAMS.				
	0 1 2 3 4 miles.				
5 M.					
20 M.					
35 M.					

To find reversely how many points $Q_{12\ldots n}$ correspond to Q_{n+1} we take arbitrarily on l the points $Q_{i+1}, Q_{i+2}, Q_{i+3}, \ldots, Q_{n+1}$ and we bring through those points respectively a $V_{i+1}, V_{i+2}, V_{i+3}, \ldots, V_{n+1}$. We now put the question how many points $Q_{123\ldots i}$ lie on l in such a way that the varieties mentioned $V_{i+1}, V_{i+2}, \ldots, V_{n+1}$ and the varieties $V_1, V_2, \ldots, V_i$ passing through $Q_{123\ldots i}$ have a common point not lying on the base-varieties. For $i < n$ the answer is: $a_1 r_1 + a_2 r_2 + \ldots + a_i r_i$.

To prove this we begin by noticing that the correctness is immediately evident for $i = 1$. If we now assume the correctness for $i = j$, we have only to show that the formula also holds for $i = j + 1$. Given the points $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$. To determine the number of points $Q_{123\ldots j+1}$ we take on l an arbitrary point $Q_{123\ldots j}$, we bring through it varieties $V_1, V_2, \ldots, V_j$ and then through each of the a_{j+1} points of intersection (not lying on the base-varieties) of these $V_1, V_2, \ldots, V_j$ and the varieties $V_{j+2}, V_{j+3}, \ldots, V_{n+1}$ resp. passing through $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$ we bring a variety V_{j+1}; these a_{j+1} varieties V_{j+1} cut l in $a_{j+1}\, r_{j+1}$ points Q_{j+1}. So to $Q_{123\ldots j}$ correspond $a_{j+1} r_{j+1}$ points Q_{j+1} and (according to the supposition that the formula holds for $i = j$) reversely to Q_{j+1} correspond $a_1 r_1 + a_2 r_2 + \ldots + a_j r_j$ points $Q_{123\ldots j}$. So there are $a_1 r_1 + a_2 r_2 + \ldots + a_j r_j + a_{j+1} r_{j+1}$ coincidences $Q_{123\ldots j}\, Q_{j+1}$; these are the points $Q_{12\ldots j\, j+1}$ belonging to the given points $Q_{j+2}, Q_{j+3}, \ldots, Q_{n+1}$; in this way the correctness of the formula has been indicated for $i = j + 1$.

When asking after the number of points $Q_{12\ldots n}$ corresponding to Q_{n+1} we have $i = n$, so that the formula furnishes $a_1 r_1 + a_2 r_2 + \ldots + a_n r_n$ for it. This number must however still be diminished by r_{n+1}, as each of the points of intersection of l with the V_{n+1} passing through Q_{n+1} is a point of coincidence $Q_{123\ldots n-1}\, Q_n$ but not one of the indicated points $Q_{12\ldots n}$.

So on l there exists between the points $Q_{12\ldots n}$ and Q_{n+1} an $(a_{n+1} r_{n+1} - r_{n+1},\ a_1 r_1 + a_2 r_2 + \ldots + a_n r_n - r_{n+1})$ correspondence. The $a_1 r_1 + a_2 r_2 + \ldots + a_{n+1} r_{n+1} - 2 r_{n+1}$ coincidences are the points of intersection of l with the locus L to be found and the points of intersection of l with the $(n-1)$-dimensional variety of contact $R V_{12\ldots n}$ of the pencils $(V_1), (V_2), \ldots, (V_n)$; we understand by that *variety of contact* the locus of the points, where the varieties $V_1, V_2, \ldots, V_n$ passing through them have a common tangent, so where the $(n-1)$-dimensional tangential spaces of those varieties cut each other according to a line.

2. To determine the order of $RV_{12\ldots n}$ we must observe that $RV_{12\ldots n}$ is the locus of the points of contact of the varieties V_n with the curves of intersection $C_{12\ldots n-1}$ of the varieties $V_1, V_2, \ldots, V_{n-1}$. So the question has been reduced to that of the order of the variety of contact of a system of ∞^1 $(n-1)$-dimensional varieties and a system of ∞^{n-1} curves. That order can be determined out of the points of intersection with an arbitrary line l.

In a point of intersection of l with a variety of the system we bring the $(n-1)$-dimensional tangential space Sp^{n-1} and in a point of intersection of l with a curve of the system the ∞^{n-2} tangential spaces Sp^{n-1}. If we act in the same way with all varieties and curves of both systems, then the tangential spaces of the varieties furnish an *1-dimensional envelope* E_1 (i. e. a curve) of *class* $\mu + \nu$ (as is evident out of its osculating spaces Sp^{n-1} through an arbitrary point of l) *with* ν *osculating spaces* Sp^{n-1} *passing through* l; here μ is the number of varieties of the system passing through an arbitrary point, and ν that of the varieties touching an arbitrary right line. The tangential spaces of the curves in the points of intersection with l have an $(n-1)$*-dimensional envelope* E_2 *of class* $\varphi + \psi$ *with* l *as* ψ*-fold line*, where φ is the number of curves of the system passing through an arbitrary point and ψ that of the curves touching an arbitrary space Sp^{n-1} in a point of a given right line of that space; for, if we bring through a point Q of l an arbitrary Sp^{n-2}, then each of the φ curves of the system passing through Q furnishes a tangential space Sp^{n-1} passing through this Sp^{n-2} whilst the space Sp^{n-1} determined by l and Sp^{n-2} (just as every other Sp^{n-1} passing through l) is ψ times tangential space of the envelope.

Both envelopes have thus $(\mu + \nu)(\varphi + \psi)$ common tangential spaces Sp^{n-1}. Each of the ν osculating spaces Sp^{n-1} of E_1 passing through l is a ψ-fold tangential space of E_2, so it counts for ψ common tangential spaces; so that $\mu\varphi + \mu\psi + \nu\varphi$ common tangential spaces not passing through l are left; these indicate by their points of intersection with l the points of intersection of l with the variety of contact, so we find:

The $(n-1)$*-dimensional variety of contact of an* ∞^1 *system of* $(n-1)$*-dimensional varieties of which* μ *pass through a given point and* ν *touch a given right line, and an* ∞^{n-1} *system of curves of which* φ *pass through a given point and* ψ *touch a given space* Sp^{n-1} *in a point of a given right line of that space, is of order*

$$\mu\psi + \nu\varphi + \mu\varphi.$$

3. With the aid of this result it is easy to determine the order

of the variety of contact (locus of the points with common tangent) of n simple infinite systems $(\mu_1, \nu_1), (\mu_2, \nu_2), \ldots, (\mu_n, \nu_n)$ of $(n-1)$-dimensional varieties.

This order is

$$\mu_1 \mu_2 \ldots \mu_n \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_n}{\mu_n} + n - 1 \right),$$

as can be shown by complete induction. The formula holds for $n = 2$. We assume the correctness of the formula for $n = i$ and out of this we must find the correctness for $n = i + 1$.

The variety of contact for $i + 1$ systems in Sp^{i+1} is the variety of contact of the system of varieties (μ_1, ν_1) and the system of curves formed by the intersections of the i remaining systems of varieties. So we have:

$$\mu = \mu_1 \quad , \quad \nu = \nu_1 \quad , \quad \varphi = \mu_2 \mu_3 \ldots \mu_{i+1}.$$

The points of contact of the curves of the system with a given space Sp^i form the $(i-1)$-dimensional variety of contact of the sections of Sp^i with the systems $(\mu_2, \nu_2), (\mu_3, \nu_3), \ldots, (\mu_{i+1}, \nu_{i+1})$; these sections are likewise systems $(\mu_2, \nu_2), \ldots, (\mu_{i+1}, \nu_{i+1})$, but of $(i-1)$-dimensional varieties. The variety of contact mentioned is according to supposition of order

$$\mu_2 \mu_3 \ldots \mu_{i+1} \left(\frac{\nu_2}{\mu_2} + \frac{\nu_3}{\mu_3} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i - 1 \right).$$

The points of intersection of that variety of contact with a right line l of Sp^i being the points of l in which Sp^i is touched by curves of the system, we have:

$$\psi = \mu_2 \mu_3 \ldots \mu_{i+1} \left(\frac{\nu_2}{\mu_2} + \frac{\nu_3}{\mu_3} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i - 1 \right).$$

Thus according to the formula $\mu\psi + \nu\varphi + \mu\varphi$ the order of the i-dimensional variety of contact of the $i + 1$ systems of varieties becomes

$$\mu_1 \mu_2 \ldots \mu_{i+1} \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_{i+1}}{\mu_{i+1}} + i \right),$$

by which the correctness of the same formula for $n = i + 1$ has been demonstrated. So we find:

For n ∞^1 systems $(\mu_1, \nu_1), (\mu_2, \nu_2), \ldots, (\mu_n, \nu_n)$ of $(n-1)$-dimensional varieties the locus of the points where the varieties of the systems passing through it have a common tangent is an $(n-1)$-dimensional variety (variety of contact) of order

$$\mu_1 \mu_2 \ldots \mu_n \left(\frac{\nu_1}{\mu_1} + \frac{\nu_2}{\mu_2} + \ldots + \frac{\nu_n}{\mu_n} + n - 1 \right).$$

If the systems are pencils, then

$$\mu_i = 1 \quad , \quad \nu_i = 2\,(r_i - 1)\,;$$

thus *the order of the variety of contact* $RV_{12\ldots n}$ *is*:

$$2\,(r_1 + r_2 + \ldots + r_n) - n - 1.$$

4. Returning to the correspondence between the points $Q_{12\ldots n}$ and Q_{n+1} we find for the number of coincidences which are points of intersection of l with the demanded locus L, i. e. for the order of L:

$$a_1 r_1 + a_2 r_2 + \ldots + a_{n+1} r_{n+1} - 2\,(r_1 + r_2 + \ldots + r_{n+1}) + \\ + n + 1 = \sum_{i=1}^{i=n+1} \{(a_i - 2)\, r_i + 1\}.$$

It is easy to see that a base-variety B_i of the pencil (V_i) is an $(a_i - 1)$-fold variety of L. The tangential spaces Sp^{n-1} of L in a point P of B_i are the tangential spaces in P of the varieties V_i, which are laid successively through one of the a_i—1 points of intersection (not lying on P and the base-varieties) of the varieties $V_1, V_2, \ldots, V_{i-1}, V_{i+1}, \ldots, V_{n+1}$ passing through P.

So we find:

Given $n+1$ *pencils* $(V_i)\,(i = 1, 2, \ldots, n+1)$ *of* $(n-1)$*-dimensional varieties in the space of operation* Sp^n. *Let* r_i *be the order of the varieties of the pencil* (V_i) *and* a_i *the number of the points of intersection (not lying on the base-varieties) of arbitrary varieties of the pencils* $(V_1), (V_2), \ldots, (V_{i-1}), (V_{i+1}), \ldots, (V_{n+1})$. *The locus proper of the pairs of points lying on varieties of each of the pencils is an* $(n-1)$*-dimensional variety of order*

$$\sum_{i=1}^{i=n+1} \{(a_i - 2)\, r_i + 1\},$$

having the $(n-2)$*-dimensional base-variety of pencil* (V_i) *as* $(a_i - 1)$*-fold variety.*

If $n > 3$, then also in the general case the base-varieties of the different pencils will intersect each other. In like manner as we have dealt with pencils of surfaces [1]) we can also determine the multiplicity of common points, curves etc. of base-varieties.

Sneek, Jan. 1907.

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[1]) See page 555.

Astromony. — "*On the astronomical refractions corresponding to a distribution of the temperature in the atmosphere derived from balloon ascents.*" Preliminary paper by H. G. VAN DE SANDE BAKHUYZEN.

1. The various theories of the astronomical refraction in our atmosphere consider the atmosphere as composed of an infinite number of concentric spherical strata, each of uniform density, whose centre is the centre of the earth and whose densities or temperatures and refractive powers vary in a definite way.

The various relations between the temperature of the air and the height above the surface of the earth, assumed in the existing theories, are chosen so, that 1st they do not deviate too far from the suppositions on the distribution of the temperature in our atmosphere, made at the time when the theory was established, 2nd that the formula derived from this relation for the refraction in an infinitesimal thin layer at any altitude could be easily integrated.

At the time when the various theories were developed, only little was known about the variations of the temperature for increasing heights, and this little was derived from the results of a small number of balloon ascents and from the observations at a few mountain-stations. In the last decade, however, ascents of manned as well as of unmanned balloons with self-registering instruments have greatly increased in number, and our knowledge of the distribution of the atmospheric temperature has widened considerably, and has become much more accurate. Now I wish to investigate, whether by means of the data obtained, we can derive a better theory of refraction, or if it will be possible to correct the results of the existing theories.

2. The temperatures in our atmosphere at different heights have been derived from the following publications:

I. Ergebnisse der Arbeiten am aëronautischen Observatorium Tegel 1900—1902, Band I, II and III.

II. Travaux de la station Franco-scandinave de sondages aëriens à Halde par Teisserenc de Bord. 1902—1903.

III. Veröffentlichungen der internationalen Kommission für wissenschaftliche Luftschifffahrt.

From the last work I have only used the observations from December 1900 till the end of 1903.

I wished to investigate the distribution of the temperature up to the greatest heights, and therefore I used for my researches only the balloon ascents which reached at least an elevation of 5000 meters;

and, following HERGESELL's advice, I have used only the temperatures observed during the ascents, as during the descents aqueous vapour may condense on the instruments.

It is evident that for the determination of the refraction, as a correction to the results of the astronomical observations, we must know the variations of the temperature at different heights with a clear sky. For the temperatures, especially of the layers nearest to the surface of the earth, will not be the same with cloudy and uncloudy weather, as in the first case the radiation of the earth will lower the temperature of those layers, and so cause an abnormal distribution of temperature. It is even possible that in the lower strata the temperature rises with increasing height, instead of lowering, as is usual.

For this reason I have divided the balloon ascents into two groups, 1st those with a cloudy sky, 2nd those with a clear or a partly clouded sky.

In working out the observations, I have supposed that for each successive kilometer's height the temperature varies proportionally to the height, and after the example of meteorologists, I have determined the changes of temperature from kilometer to kilometer. For this purpose, I have selected from the observations, made during each ascent, the temperature-readings on those heights, which corresponded as nearly as possible with a round number of kilometers, and I have derived the variations of temperature per kilometer through division.

The available differences of height were often less than a kilometer, especially at the greatest elevations; in those cases I adopted for the weight of the gradient a number proportional to the difference of heights. Sometimes on the same day, at short, intervals several ascents have been made at the same station, or at neighbouring stations, from which the variations of temperature at the same heights could be deduced. In these cases I have used the mean of the results obtained, but I assumed for that mean result the same weight as for a single observation, as the deviations of the daily results from the normal distribution of temperature are only for a small part due to the instrumental errors, and for the greater part to meteorological influences.

3. The observations which I have used, were the following: from publication I, 31 ascents of which 12 had been made in pairs on the same day, so that 25 results were obtained; from publication II, 38 ascents all on different days; and from publication III, 170

ascents distributed over 119 different days; — I have disregarded the observations marked as uncertain in this work. On the whole I have obtained the results on 182 different days, of which 58 with unclouded and 124 with clouded sky.

The temperature gradients for each month were derived from this material, and to obtain a greater precision, I have combined them in four groups, each of three successive months, December, January and February (winter), March, April and May, (spring), June, July and August, (summer), September, October, November, (autumn).

TABLE I.

Variations of temperatures per kilometer.

(V.T. Variation of temperature per kilometer; N. Number of observations).

A. Clear sky.

	Winter.		Spring.		Summer.		Autumn		Mean.	
Kil	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.
0— 1	+ 1.2°	10	— 3.6°	15	— 2.8°	18	+ 0.6°	15	— 0.6°	58
1— 2	— 4.2	10	— 5.4	15	— 4.3	18	— 3.2	15	— 4.3	58
2— 3	— 5.2	10	— 4.9	15	— 4.4	18	— 4.6	15	— 4.7	58
3— 4	— 5.4	10	— 5.8	15	— 5.4	18	— 5.3	15	— 5.5	58
4— 5	— 5.3	10	— 6.7	14.3	— 5.9	18	— 5.7	14.9	— 5.9	57.2
5— 6	— 5.6	8.9	— 7.1	13.6	— 6.0	18	— 7.3	13.8	— 6.5	54.3
6— 7	— 5.8	8	— 7.5	12.7	— 6.6	17.3	— 6.7	10.1	— 6.7	48.1
7— 8	— 6.8	7	— 7.8	10.8	— 7.5	14.6	— 8.0	8	— 7.5	40.4
8— 9	— 7.6	5	— 6.4	7.8	— 7.4	13.3	— 8.1	8	— 7.3	34.1
9—10	— 5.9	4	— 4.4	5.7	— 7.2	13	— 6.9	7	— 6.4	29.7
10—11	— 3.8	2.9	— 2.5	5	— 6.8	10.4	— 6.1	6.8	— 5.4	25.1
11—12	— 6 2	2	— 2.4	2.6	— 5.9	5.2	— 2.0	5.9	— 3.5	15.7
12—13	— 1.6	2	+ 2.0	1	— 1.1	2	— 1.0	4.9	— 0.7	9.9
13—14			+ 7.0	1	+ 1.0	2	— 4.0	1.6	— 0.8	4.6
14—15					+ 0.7	1.6	— 5.1	1	— 1.5	2.6
15—16					+ 0.8	1			+ 0.8	1

B. Cloudy sky.

	Winter.		Spring.		Summer.		Autumn.		Mean.	
Kil.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.	V.T.	N.
0— 1	— 1°.8	27	— 5°.5	33	— 3°.7	24	— 3°.9	40	— 3°.8	124
1— 2	— 3.0	27	— 5.6	32.5	— 5.1	24	— 3.7	49	— 4.3	123.5
2— 3	— 4.5	27	— 4.8	33	— 5.1	24	— 4.3	40	— 4.5	124
3— 3	— 5.8	27	— 5.5	33	— 5.1	23.8	— 5.8	39.5	— 5.6	123.3
4— 5	— 6.8	27	— 6.7	33	— 6.1	23	— 6.1	39	— 6.4	12.2
5— 6	— 6.9	26	— 6.7	30.7	— 6.7	21.5	— 6.2	36.5	- 6.6	114.7
6— 7	- 6.8	25.4	— 6.7	25	— 6.6	17.7	— 7.3	27.8	— 6.9	95.9
7— 8	— 6.9	19.7	— 7.2	20.3	— 7.2	16.8	— 5.9	21.6	— 6.8	78.4
8— 9	— 6.1	14.2	— 6.0	16.2	— 7.9	14.1	— 7.9	13	— 6.9	57.5
9—10	— 6.2	12.3	— 3.9	12.9	— 8.4	12.1	— 7.5	11.4	— 6.5	48.7
10—11	— 5.4	9.4	— 1.8	9.6	— 5.9	8.1	— 5.4	8.5	— 4.5	35.6
11—12	— 2.5	7.6	+ 1.0	8.3	— 2.1	5.1	— 1.9	6.8	— 1.2	27.8
12—13	— 1.3	5	+ 1.2	6.7	+ 0.2	1.9	— 0.5	4.1	+ 0.1	17.7
13—14	— 0.9	2.7	— 3.9	1			+ 1.7	1.4	— 0.8	5.1
14—15	+ 1.9	1.9	— 3.2	1					+ 0.2	2.9
15—16	— 0.6	1	— 3.2	0.5					— 1.5	1.5
16—17	+ 0.1	0.8							+ 0.1	0.8

We may derive from these tables that the mean variation of temperature with clear and with cloudy weather only differs in the lower strata, but is nearly the same in the higher ones.

In order to deduce from the numbers in this table the temperatures themselves from kilometer to kilometer, I have also derived from the data the following mean temperatures at the surface of the earth:

	clouded sky	clear sky
Winter	+ 0°.1	— 0°.9
Spring	+ 6 .4	+ 5 .1
Summer	+ 14 .4	+ 14 .7
Autumn	+ 9 .0	+ 7 .9

By means of these initial temperatures and the gradients of table I

C. Cloudy and uncloudy sky.

	Winter.			Spring.			Summer.			Autumn.			Mean.		
Kil.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.	V.T.	N.	Hann.
0— 1	—1°.0	37	+0°.5	—3°.8	48	—3°.1	—3°.3	42	—4°.1	—2°.7	55	—2°.1	—2°.8	182	—2°.2
1— 2	—3.3	37	—2.2	—5.6	47.5	—5.5	—4.7	42	—5.6	—3.6	55	—4.1	—4.3	181.5	—4.4
2— 3	—4.7	37	—5.0	—4.9	48	—5.1	—4.8	42	—5.1	—4.4	55	—4.8	—4.7	182	—5.0
3— 4	—5.7	37	—5.8	—5.6	48	—5.8	—5.2	41.8	—5.6	—5.6	54.5	—5.8	—5.5	181.3	—5.7
4— 5	—6.4	37	—6.7	—6.7	47.3	—6.7	—6.0	41	—5.9	—6.0	53.9	—5.9	—6.2	179.2	—6.3
5— 6	—6.7	34.9	—6.7	—6.8	44.3	—7.3	—6.4	39.5	—6.4	—6.5	50.3	—6.8	—6.6	169	—6.8
6— 7	—6.6	33.4	—6.7	—7.0	37.7	—7.2	—6.6	35	—7.2	—7.1	37.9	—7.1	—6 9	144	—7.0
7— 8	—6.9	26.7	—7.2	—7.4	31.1	—6.3	—7.4	31.4	—7.7	—6.4	29.6	—7.3	—7.3	118.8	—7.1
8— 9	—6.5	19.2	—6.9	—6.1	24	—6.4	—7.6	27.4	—7.6	—7.9	21	—7.6	—7 1	91.6	—7.1
9—10	—6.2	16.3	—6.4	—4.0	18.6	—4.8	—7.8	25.1	—6.9	—7.4	18.4	—6.6	—6.5	78.4	—6.3
10—11	—5.0	12.3	—3.9	—2.0	14.6	—0.9	—6.4	18.5	—5.0	—5.7	15.3	—6.1	—4.9	60.7	—4.0
11—12	—2.6	9.6	0.0	—0.2	10.	+0.5	—4.0	10.3	—2.4	—1.9	12.7	—2.7	—2.1	43.5	—1.2
12—13	—1.2	7		+1.3	7.7		—0.5	3.9		—0.5	9		—0.2	27.6	
13—14	—0 9	2.7		—1.6	2		+1.0	2		—1.3	3		—0 8	9.7	
14—15	+1.9	1.9		—3.2	1		+0.7	1.6		—5.1	1		—0 6	5.5	
15—16	—0.6	1		—3.2	0.5		+0.8	1					—0.6	2.5	
16—17	+0.1	0.8											+0.1	0.8	

which in a few cases have been slightly altered, I have derived the following list of temperatures for clear weather from kilometer to kilometer.

Although the adopted values for the temperature of the air above 13 kilometer are not very certain, yet the observations indicate that at these heights the temperature decreases slowly with increasing height. The refraction in those higher strata being only a small part of the computed refraction, nearly $^1/_{10}$, an error in the adopted distribution of temperature will have only a slight influence on my results.

I must remark that almost all the observations have been made during the day, generally in the morning. It is evident that the variation of temperature, especially near the surface of the earth, is not the same during the day and during the night, but the number of

TABLE II.

Temperatures at heights from 0 to 16 kilometer for clear weather.

	Winter.		Spring.		Summer.		Autumn.		Mean.	
Height.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.	Temp.	Diff.
0	— 1°9		+ 5°1		+14°7		+ 7°9		+ 6°4	
		+1.2		—3.6		—2.8		+0.6		—1.1
1	— 0.7		+ 1.5		+11.9		+ 8 5		+ 5.3	
		—4.2		—5.4		—4.3		—3.2		—4.3
2	— 4.9		— 3.9		+ 7 6		+ 5.3		+ 1.0	
		—5.2		—4.9		—4.4		—4.6		—4 8
3	—10.1		— 8.8		+ 3.2		+ 0.7		— 3.8	
		—5.4		—5.8		—5.4		—5.6		—5.5
4	—15.5		—14 6		— 2.2		— 4.9		— 9.3	
		—5.8		- 6.7		—5.9		—6.1		—6 1
5	—21.3		—21.3		— 8.1		—11.0		—15 4	
		— 6.0		—6.7		—6.0		—6.9		—6 4
6	—27.3		—28.0		—14.1		—17.9		—21.8	
		—6.2		—6.9		—6.6		—7.2		—6.7
7	—33 5		—34.9		- 20.7		- 25.1		—28.5	
		—6.8		—7 3		—7.3		—7.7		—7.3
8	—40.3		—42.2		—28.0		—32.8		—35.8	
		—7.3		—6.9		—7.6		—7.6		—7.4
9	—47.6		—49.1		—35.6		-40.4		- 43.2	
		—6.4		—5.4		—7.2		—6.9		—6.4
10	—54.0		—54 5		—42 8		—47.3		—49 6	
		—4.9		—2 5		—6.8		—6.1		—5.1
11	—58.9		—57.0		—49.6		—53.4		—54 7	
		—2.1		—1 0		—4.0		—2 0		- 2.3
12	—61.0		—58.0		—53.6		—55.4		—57.0	
		—1.0		—1.0		—1.0		—1.0		—1.0
13	—62.0		—59.0		—54.6		—56 4		—58 0	
		—0.6		—0.6		—0.6		—0.6		—0.6
14	—62.6		—59 6		—55.2		—57.0		—58.6	
		—0.4		—0.4		—0.4		—0.4		—0.4
15	—63.0		—60.0		—55.6		—57.4		—59.0	
		—0.2		—0.2		—0.2		—0.2		—0.2
16	—63 2		—60.2		—55.8		—57.6		—59.2	

observations was not great enough for a *reliable* determination of this difference. Lastly I remark that the various balloon ascents have been made from different stations, Halde (in Danemark), Berlin, Paris, Strasbourg and Vienna and consequently the given values do not hold for one definite place, but for the mean of the *area* enclosed by those stations.

After I had derived the temperatures given in table II, I got notice of two papers, treating of about the same subject, namely: J. Hann, Ueber die Temperaturabnahme mit der Höhe bis zu 10 Km. nach den Ergebnissen der internationalen Ballonaufstiege. Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der K. K. Akademie der Wissenschaften Wien. Band 93, Abth. IIa, S. 571; and S.

GRENANDER. Les gradients verticaux de la température dans les minima et les maxima barométriques. Arkiv för Matematik, Astronomi och Fysik. Band 2. Hefte 1—2 Upsala, Stockholm.

Of the results which HANN has given, up to a height of 12 kil., I have taken the means of groups of 3 months, which are printed in table I by the side of the values I had obtained; the agreement of the two results, which for the greater part have been deduced from different observations, is very satisfactory.

GRENANDER in his paper chiefly considers the relation between the changes of temperature and the barometer readings; his results cannot therefore be compared with mine directly, but probably we are most justified in comparing the variations of temperature at barometer maxima, with those which I have computed for clear weather. For great elevations, till nearly 16 kil., GRENANDER also obtains with increasing height a small decrease of temperature.

It is difficult to state with what degree of precision the temperatures of table II represent the mean values for the different seasons; the deviations, especially at great heights, may perhaps amount to some degrees, but certainly they represent the mean distribution of temperature better than the values adopted in the various theories of refraction, and we can therefore derive from them more accurate values for the refraction.

4. It is hardly possible to represent the relation between the temperatures in table II and the heights by a simple formula, and to form a differential equation between the refraction, the zenith distance and the density of the atmosphere at a given height, which can be easily integrated.

Therefore I have followed another method to determine the refraction corresponding to the distribution of temperature I had assumed.

According to RADAU's notations (Essai sur les réfractions astronomiques. Annales de l'Observatoire de Paris. Mémoires Tome XIX), the differential equation of the refraction, neglecting small quantities, is:

$$ds = \alpha'' \frac{\left(1 - \frac{l_0}{R}(y - 3\,\varepsilon\omega)\right) d\omega}{\sqrt{\left\{\cot^2 z + 2\frac{l_0}{R}(y - \varepsilon\omega) - \left(\frac{l_0}{R}y - 2\frac{l_0}{R}\varepsilon\omega\right)^2\right\}}} \quad (I)$$

Here is:

R radius of the earth for 45° latitude,

r_0 radius of the earth for a given point,

h height above the surface of the earth,

$r = r_0 + h$,
μ_0 index of refraction at the surface of the earth,
μ „ „ „ „ „ height h,
ϱ_0 density of the air at the surface of the earth,
ϱ density at the height h,
t_0 temperature at the surface of the earth,
l_0 height of a column of air of uniform density at 45° latitude, of a temperature t_0, which will be in equilibrium with the pressure of one atmosphere, the gravity being the same at different heights. According to REGNAULT's constants, we have $l_0 = 7993\ (1 + \alpha t_0)$ meter, if α represents the coefficient of expansion of the air.

Between these quantities exist the following relations:

$$\mu^2 = 1 + 2c\varrho \ (c \text{ being a constant}), \quad \omega = 1 - \frac{\varrho}{\varrho_0}$$

$$a = \frac{c\varrho_0}{1+2c\varrho_0} \qquad a'' = \frac{a}{\sin 1''} \qquad \varepsilon = \frac{R}{l_0}\,a \qquad y = \frac{Rh}{(r_0+h)l_0}.$$

To determine the value of ds at each height, we require a relation between ω and y or between ω and h, which can be obtained when we assume that the temperature varies according to IVORY's theory, or that the temperature varies as represented in table II. For the same given values of z and ω, the two values of ds in formula (I) can be computed by means of the first and by means of the second supposition, and the differences of these two values of ds can be found. By means of mechanical quadrature, we can then determine the differences Δs of the refractions s according to IVORY's theory and according to table II.

The relations between y and ω may be found in the following manner.

5. If in a given horizontal initial plane, at a distance r_0 from the centre of the earth, the pressure is p_0, the temperature t_0 and the density of the air ϱ_0, and in another horizontal plane, h kil. above the former, the pressure is p, the temperature t, the distance from the centre of the earth r, and the density of the air ϱ, then we have (see RADAU):

$$l_0\, d\left(\frac{p}{p_0}\right) = -\frac{\varrho}{\varrho_0}\left(\frac{R}{r}\right)^2 dh = -\frac{\varrho}{\varrho_0}\frac{R}{r_0}\, d\left(\frac{Rh}{r}\right), \text{ or } \frac{r_0}{R}\, d\left(\frac{p}{p_0}\right) = -\frac{\varrho}{\varrho_0}\, d\left(\frac{Rh}{l_0 r}\right),$$

or, putting $\frac{\varrho}{\varrho_0} = \eta$ and $\frac{Rh}{(r_0+h)\,l_0} = y$:

$$\frac{r_0}{R}\, d\left(\frac{p}{p_0}\right) = -\eta\, dy; \qquad \ldots\ldots\ldots \text{(II)}$$

further is:

$$\frac{p}{p_0} = \frac{1+at}{1+at_0}\,\eta = \left(1 - \frac{a\,(t_0-t)}{1+at_0}\right)\eta = (1-\vartheta)\,\eta, \quad . \quad . \quad \text{(III)}$$

if we put $\frac{a\,(t_0-t)}{1+at_0} = \vartheta$.

When dividing equation (II) by (III), we get:

$$\frac{r_0}{R}\,\frac{d\left(\frac{p}{p_0}\right)}{\frac{p}{p_0}} = -\frac{dy}{1-\vartheta},$$

while by differentiating logarithmically we find:

$$\frac{d\left(\frac{p}{p_0}\right)}{\frac{p}{p_0}} = -\frac{d\vartheta}{1-\vartheta} + \frac{d\eta}{\eta}.$$

From the two last equations follows:

$$dy = \frac{r_0}{R}\left\{d\vartheta - (1-\vartheta)\,\frac{d\eta}{\eta}\right\} = \frac{r_0}{R}\left\{d\vartheta + (1-\vartheta)\,\frac{d\omega}{1-\omega}\right\}. \quad . \quad \text{(IV)}$$

According to IVORY's theory $\vartheta = f\omega$, where f is a constant value (RADAU assumes 0,2); if we introduce this relation into the equation (III) we obtain after integration:

$$y = 0{,}4\,\frac{r_0}{R}\,\omega - 1{,}8420681\,\frac{r_0}{R}\,Br.\,log\,(1-\omega) \quad . \quad . \quad . \quad \text{(V)}$$

By substituting (V) in (I) we can therefore calculate for each value of ω the value of ds according to IVORY's theory.

6. Now I proceed to determine the relation between ω and y according to the temperature table II.

Of two horizontal planes, one above the other, the first is situated n kil. (n a whole number), the second n' kil. ($n' =$ or $< n+1$) above the surface of the earth; their distances from the centre of the earth are r_n and $r_{n'}$, their temperatures t_n and $t_{n'}$ and the values of y, y_n and $y_{n'}$. The temperature between n and n' varies regularly with the height and, to simplify the formulae, I suppose $t_n - t_{n'}$ proportional to $y_{n'} - y_n$, so that, if $\vartheta_n = \frac{a\,(t_n - t_{n'})}{1+at_n}$:

$$\frac{R}{r_n}\,(y_{n'} - y_n) = c_n\,\vartheta_n. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(VI)}$$

Hence follows $\frac{R}{r_n}\,dy = c_n\,d\vartheta$ and after substitution of dy in (IV)

and integration

$$(c_n - 1)\, lg\,(1 - \vartheta_n) = lg\,(1 - \omega) \quad . \quad . \quad . \quad . \quad \text{(VII)}$$

in which $1 - \omega$ represents the ratio of the densities in the two horizontal planes.

If we substitute $n + 1$ for n', we can find in table II the temperature for the two planes and hence also ϑ_n; as y_n and y_{n+1} are also known, we can derive from (VI) the value of c_n and we can deduce from (VII) the ratio of the densities in those planes. By putting for n successively 0, 1, 2, etc. we can construct a table containing the densities of the air, D_1, D_2, D_3 etc. at the height of 1, 2, 3, etc. kil. above the surface of the earth, the density at the surface being unity.

It is easy to derive from this table the height of a layer of a given density d. If $d < D_n$ and $> D_{n+1}$, the layer must be situated between n and $n + 1$ kil., and we only want to know in which manner, within this kil., the density varies with the height h above the lower plane.

We may assume:

$$\frac{d}{D_n} = 10^{-ah}.$$

For $h = 1$ kil., $d = D_{n+1}$, hence $a = -\,lg \dfrac{D_{n+1}}{D_n}$.

a being known, we may determine for each value of d, h and also y. By substitution in (I) we find then for each value of ω the value of ds.

7. Now we are able to form the differences of ds after the theory of Ivory and after the table of temperatures II, for values of ω which increase with equal amounts, and then determine the whole difference of the refraction for both cases.

For great values of z and small values of y and ω the coefficients of $d\omega$ in (I) will become rather large, which derogates from the precision of the results.

This will also be the case when the differences of the successive values of ω are large; small differences are therefore to be preferred, but they render the computation longer.

Both these difficulties can be partly avoided if, according to Radau's remark, we introduce $\sqrt{\omega}$ as a variable quantity instead of ω; the value of ds thus becomes:

$$ds = \frac{a''}{\sqrt{\frac{l_0}{2R}}} \frac{\left(1 - \frac{l_0}{R}(y - 3\varepsilon\omega)\right) d\sqrt{\omega}}{\sqrt{\left\{\frac{\frac{R}{2l_0}\cot^2 z + y}{\omega} - \varepsilon - \frac{l_0}{2R\omega}(y - 2\varepsilon\omega)^2\right\}}} \quad \text{(VIII)}$$

or approximately:

$$ds = \frac{a''}{\sqrt{\frac{l_0}{2R}}} \frac{d\sqrt{\omega}}{\sqrt{\left\{\frac{\frac{R}{2l_0}\cot^2 z + y}{\omega} - \varepsilon\right\}}}$$

It is evident that for small values of ω the coefficient of $d\sqrt{\omega}$ in (VIII) is smaller than that of $d\omega$ in (I), and that also the refraction in the lower strata will be found more accurately by means of the formula (VIII) than by means of (I). For if we increase $\sqrt{\omega}$ in formula (VIII) and ω in formula (I) with equal quantities, beginning with zero, we find, that, from $\omega = 0$ to $\omega = 0{,}2$, the number of values in the first case is twice as great as in the second case, hence the integration by means of quadrature will give more accurate results in the first case.

Therefore I have used the formula (VIII) and computed the coefficient of $d\sqrt{\omega}$ for values of $\sqrt{\omega}$, 0, 0,05, 0,10, 0,15 ... to 0,95.

The density of the air which corresponds to $\sqrt{\omega} = 0{,}95$, occurs at the height of about 18 kil. From the observations at my disposal I could not deduce reliable values for the temperature at heights above 16 kil.; yet it is probable that the gradients at those heights are small and I have assumed the temperature at heights of 17 and 18 kil. to be equal to that at a height of 16 kilometers.

In this way I have determined by means of mechanic quadrature, and an approximate computation of the refraction between $\sqrt{\omega} = 0.925$ and $\sqrt{\omega} = 0.95$, the differences Δs of the two values of the refraction corresponding to IVORY's theory and corresponding to the table of temperature II in the part of the atmosphere between the earth's surface and a layer at a height of about 18 kil. where $\sqrt{\omega}$ is 0.95. I have worked out this comptuation for the zenith distances 85°, 86°, 87°, 88°, 88°30′, 89°, 89°20′, 89°40′ and 90°.

An investigation, made for the purpose, showed me that in formula (VIII) the terms $\frac{lo}{R}(y - 3\varepsilon\omega)$ in the numerator and $\frac{lo}{2R\omega}(y - 2\varepsilon\omega)^2$ in the denominator may be neglected for all zenith distances except $z = 90°$; therefore I have taken them into account in the computation of the horizontal refraction only.

The results which I have obtained for the differences:

Δs = IVORY—table of temperatures

are the following:

TABLE III.

Refraction after IVORY — Refractions after the table of temperatures II.

Zenith distance	Winter	Spring	Summer	Autumn	Annual mean	Annual mean — Winter	Annual mean — Spring	Annual mean — Summer	Annual mean — Autumn
85°	+ 0″21	+ 0″78	+ 0″66	+ 0″31	+ 0″49	+ 0″28	− 0″29	− 0″17	+ 0″18
86°	+ 0.13	+ 1.26	+ 0.95	+ 0.30	+ 0.66	+ 0 53	− 0.60	− 0.29	+ 0.36
87°	− 0.47	+ 2.08	+ 1.31	− 0.20	+ 0 66	+ 1 13	− 1.42	− 0.65	+ 0.86
88°	− 3 93	+ 3.10	+ 0.95	− 3.29	− 0.83	+ 3 10	− 3.93	− 1.78	+ 2.46
88°30′	− 9.64	+ 3.06	− 0.67	− 8.51	− 3.95	+ 5.69	− 7.01	− 3.28	+ 4.56
89°	−23.69	+ 1.08	− 5.45	−21.15	−12.31	+11.38	−13.39	− 6 86	+ 8.84
89°20′	−43.80	− 3.17	−12 68	−38.77	−24.51	+19.29	−21 34	−11.83	+14.26
89°40′	−1′ 21″97	−13.07	−25.25	−1′ 11″16	−27.74	+34.23	−34.67	−22.49	+23.42
90°	−2 32.4	−33.1	−52.9	−2 9.6	−1′ 30″9	+1′ 1″5	−57.8	−38.0	+38.7

To test the computations, we may compare the mean of the values of Δs for the four seasons, and the values of Δs in column 6 which have been computed, independently the former, for the mean yearly temperatures, which are almost equal to the mean of the temperatures in the four seasons. Only for $z = 89°40'$ and $z = 90°$ do these values show deviations exceeding 0″.1.

From table III follows, 1 that for a distribution of temperature, as derived by me from observations, the refraction deviates perceptibly from that deduced from IVORY's theory, 2 that the differences in the refraction in the different seasons are about of the same order as the deviations themselves. I want it to be distinctly understood, 1 that the adopted distribution of temperature above 13 kil. and especially from 16 to 18 kil. is uncertain, and 2 that I have not taken into account the refraction in the layers which are lying more than 18 kil. above the surface of the earth, in other words those layers where the density, as compared to that of the surface of the earth, is less than $1 - 0{,}95^2$, or less than 0,0975.

Physiology. — "*An investigation on the quantitative relation between vagus stimulation and cardiac action, on account of an experimental investigation of* Mr. P. WOLTERSON" [1]). By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of December 29, 1906).

The experiments were performed on Emys orbicularis, whose right nervus vagus was stimulated by means of condensator charges and non-polarising electrodes of DONDERS [2]), while auricle and ventricle were recorded by the suspension method. The mica-condensators had a capacity of 0,02, 0,2 and 1 microfarad, the voltage varied from a fraction of a volt to 12 volts, occasionally even more. From this the intensity of the stimulus was calculated in ergs (or in coulombs by HOORWEG's method). Only a part of this energy, passing through the nerve, when it is charged, acts as a stimulus. What part this is remains unknown, but it is supposed not to vary too much in the same set of experiments. In the typical experiments a summation took place of ten stimuli, succeeding each other in tempos of $^1/_2$ second; in particular experiments single stimuli or other summations were investigated. Of fatigue little evidence is found with our mode of experimenting, rather a somewhat increased sensitiveness of the vagus system towards the end of a set of experiments.

Stimulation of the right vagus produces in the tortoise in the first place lengthening of the duration of a cardiac period [3]), in such a way that in the second period, after a stimulus, starting during the cardiac pause, the diastolic half of the period is considerably retarded, while in some subsequent periods a decreasing retardation of the diastolic part of the period is noticed.

Then stimulation of the vagus causes contraction to become feebler, this phenomenon becoming gradually more distinct and reaching its maximum some periods after stimulation. This decrease of contractile power is primary, since it may also occur when any change in the automatic action is absent (e.g. when the stimulus consists of one condensator charge and when the left vagus is stimulated). Finally vagus stimulation as a rule produces slackening of the tonus, rarely tonic heightening. Changes in conductivity were only observed once.

[1]) For details we refer to the author's academical thesis, which will be published ere long.

[2]) Onderzoekingen Phys. Lab. Utrecht (3) Vol I p. 4, Pl. I, fig. 1, 1872.

[3]) The duration of a cardiac period is reckoned from the foot-point of a sinusal contraction or if this is not visible, of an auricular contraction, to the foot-point of the next following sinusal resp. auricular contraction.

The negative chronotropy holds good for sinus, auricle and ventricle to the same extent, the negative inotropy exists exclusively for the sinus and the auricle, is mostly positive for the ventricle, if it is found; the tonotropy is met with in auricle and ventricle.

A latent stage of the phenomenon, measured by the time-difference between vagus stimulation and vagus action, was always observed. It is smallest for the inotropy; already the first period often shows an enfeeblement of the contraction, which in the subsequent periods increases still further. The latent stage of the chronotropy is greater, for only in the second, sometimes in the third period, a retardation is noticeable; on the other hand this phenomenon reaches its maximum at once. Inotropy and tonotropy do not coincide. On the contrary, the maxima of effect form the following series as to time: first maximum of chronotropy, then maximum of tonotropy, finally maximum of inotropy.

In regard to the sensitiveness for vagus stimuli, we remark that for the inotropy the "threshold value" lies below that for the chronotropy and for this latter lower again than for the tonotropy. So we have:

Threshold value for inotropy $<$ idem for chronotropy $<$ idem for tonotropy.

From the fact that dromotropy did not occur in our experiments, one would infer that the threshold value of the dromotropy lies higher still in the present case.

Physiologists are generally convinced that the rhythmic processes at the bottom of the cardiac pulsations, are based on chemical actions in the cardiac muscle. Leaving apart the founder of the myogenic theory TH. W. ENGELMANN, we mention some authoritative writers, FANO and BOTAZZI in RICHET's Dictionnaire and HOFMANN in NAGEL's Handbuch, who embrace this point of view [1]).

Also experimental results may be adduced in support of this theory. SNYDER [2]) showed that the frequency of the contractions with respect to temperature follows exactly the law, formulated by VAN 'T HOFF and ARRHENIUS for chemical reactions [3]) and experiments, independently made by J. GEWIN, entirely confirmed this. [4]) Whereas the influence of temperature is considerable, that of pressure is very small. This agrees with the small significance of external pressure for so-called condensed systems, i. e. systems in which no gaseous phases occur.

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1) FANO and BOTAZZI, RICHET's Dict. de physiologie t. IV. p. 316.

2) SNYDER, Univ. of California Publications II. p. 125. 1905.

3) E. COHEN, Voordrachten. Blz. 236 1901.

4) J. GEWIN, Onderzoekingen Physiol. Lab. Utrecht (5). Dl. VII, p. 222.

For the automatism it seems to me to be settled, that it must be based on chemical processes.

For the remaining cardiac properties: conductivity, local sensitiveness to stimuli, contractile power and tonicity the decision is more difficult. The law of VAN 'T HOFF-ARRHENIUS concerning the relation between reaction-velocity and temperature can only be applied if the duration of the reaction is known. Now the velocity of conduction, measured with this purpose, increases with temperature up to a certain optimum [1]) whereas correspondingly the duration of the contractions is diminished [2]). The local excitability, however, has not been studied yet from this point of view, while also for the contractile power the time factor is still lacking. But the contraction of a muscle and also that of the cardiac muscle is so universally considered a truly chemical process, that the reader will not object to classing it among chemical phenomena without further arguments. As to the tonicity we are absolutely in the dark, although we know that rise of temperature chiefly brings about a change, in which the tonus is definitely abolished.

In preparing his thesis Mr. WOLTERSON had chiefly to deal with:

1. changes in the automatism (chronotropy);
2. changes in the contractile power (inotropy).

Both these changes are purely chemical phenomena, as was shown above.

For chemical processes the law of GULDBERG and WAAGE holds [3]), and we may apply this law to the processes here dealt with. For this purpose we shall have to give a nearer definition for our special case of the conception "times of equal change".

By "times of equal change" we mean the times in which a definite reaction has taken place between two accurately fixed and in the corresponding cases analogous terminal points. The total duration of a cardiac period is such a characteristic time element, the beginning and end of which cannot be determined with the balance after chemical analysis, but still are determined by biological characteristics. The time between the beginning and the end of a cardiac period may be looked upon as a time of equal change provided no

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[1]) TH. W. ENGELMANN. Onderz. Physiol. Lab. Utrecht (3d series) III p. 98. Above the optimum the conductive velocity diminishes again.

[2]) HOFMANN l. c. p. 247. Recently confirmed by V. E. NIERSTRASZ; vide acad. thesis, Utrecht 1907, p. 145, fig. 22: a fall in temperature of 9° gave an increase of the duration of the systole to the double value.

[3]) E. COHEN. Ned. Tijdschr. v. Geneesk. 1901, Vol. I, p. 58. Cf. also ZWAARDEMAKER, ibidem, 1906. Vol. II. p. 868.

inotropic changes occur [1]) and the mechanical resistance which the heart has to overcome, has remained the same.

These premisses made, we may at once apply the fundamental equation of GULDBERG and WAAGE's law;

$$\varphi = kC^n$$

Here k is a constant, the constant of the reactional velocity, C is the quantity of the substance, taking part in the reaction, n is the exponent, determining the so-called order of the reaction, while φ indicates the reactional velocity. About the exponent n nothing can be stated a priori for the heart. Toxicological experiments, in which the quantity of the reacting substance diminishes, might perhaps teach us something in this respect; perhaps also experiments on fatigue might give us some clue; at present, however, no data at all are available. Whether there are intermediate reactions and in what number, cannot be ascertained. Under these circumstances I assume, quite arbitrarily, that the present case is the simplest and that the exponent is unity. If later this assumption turns out to be wrong, our calculations will still apply, mutatis mutandis, without losing their meaning. In this simple case the formula runs:

$$\varphi = k\,C.$$

When the vagus is stimulated a very marked alteration of the times of equal change is noticed. The reactional velocity of the hypothetical chemical process, which lies at the bottom of the automatism, must consequently undergo a very considerable change. Such a change cannot take place unless either k or C are modified. In the literature on the subject both views are put forth, but only the conception that k changes, leads to a clear explanation without further auxiliary hypotheses. It also fits in best with a recent paper of MARTIN [2]), according to which vagus-inhibition is ascribed to the action of K-ions and is counter-acted by rise of temperature. The significance of the ions of the alkalies and alkaline earths for the cardiac muscle is indeed by no means fully explained, even after the mumerous investigations of J. LOEB and his followers and critics — they are regarded by some as the cause of the continually excited condition of the cardiac muscle, as the stimulus for the automatism [3]), by others as the condition, necessary for keeping the

[1]) In the ventricle vagus-stimulation produces no inotropy.

[2]) MARTIN. Amer. Journal of Physiol. Vol. XI, p. 370, 1904 (MARTIN himself seems to assume a compound of K-ions with C).

[3]) WENCKEBACH. Die Arythmie etc. Eine physiol.-klinische Studie. Leipzig. 1904.

active substances in solution [1]) — they certainly do not enter into simple chemical combination with the cardiac substance, by which this latter would become unfit. If this latter were the case, the life-prolonging influence of RINGER's solution and the remarkable antagonism of *Na* and *K* on one hand and *Ca* on the other, would be entirely unexplainable.

By placing the principal weight on the hypothesis that the vagus alters the constant of velocity, of reaction we were led to the application of the formula for the catalytic acceleration of a chemical reaction. The catalytic acceleration is here negative. The explanation of the formula will be found in G. BREDIG's work. It runs:

$$\beta = k' - k = \frac{1}{(t'_2 - t'_1)} - \frac{1}{(t_2 - t_1)}.$$

By application to our experiments, the normal duration of the period being indicated by $(t_2 - t_1)$ the altered one during the principal retardation by $(t'_2 - t'_1)$, a relation became evident which appears to be constantly found between the intensity of the vagus stimulus on one hand and the retardation, indicated by β on the other. (An examination of the curves, recorded by the heart would show that the retardation affects principally the diastolic part of the process, but since for this part, taken separately, the times of equal change cannot be sharply determined, our calculations enclose the whole process).

When the vagus stimulus increases the retardation increases also very gradually, until a definite degree is reached; from this moment the reactional velocity of the hypothetical process of the automatism remains the same, independent of any rise in the intensity of the stimulus. Only by increase of the duration of the vagus stimulus, a new retardation may be produced, which is pretty well proportional to the extension of the duration of the stimulus. For a warmed heart all this holds without any alteration.

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[1]) H. J. HAMBURGER. Osmotischer Druck und Ionenlehre. Bd. III, p. 127.

Exp. 8, VI. 1906. Emys orbicularis. Right nervus vagus stimulated on non-polarising electrodes with charging currents. Capac. of the condensator 1 microfarad. Number of stimuli 10 (2 per second). Between the series of stimuli pauses of 4 minutes; external temperature 18° C.

Micro-coulomb	Ergs	Initial retard. in %	Total retard. in %	β
0.80	3.20	13	23	—0.0392
0.82	3.36	92	143	—0.1662
0.84	3.53	95	133	—0.1694
0.86	3.69	282	347	—0.2555
0.88	3.87	320	385	—0.2716
0.90	4.05	320	364	—0.2635
0.92	4.23	322	360	—0.2648
0.94	4.42	346	364	—0.2765
0.96	4.61	337	366	—0.2575
0.98	4.80	337	398	—0.2667
1.00	5.00	343	398	—0.2679
1.04	5.41	333	394	—0.2570
1.08	5.83	346	410	—0.2765
1.12	6.27	333	367	—0.2661
1.20	7.20	330	322	—0.2480
1.28	8.19	346	373	—0.2592
1.36	9.25	336	370	—0.2575
1.52	11.50	343	374	—0.2679
1.68	14.11	360	421	—0.2790
1.84	16.93	340	377	—0.2673
3.68	67.71	371	405	—0.2723
5.52	152.35	371	418	—0.2723
7.36	270.85	371	411	—0.2723
9.20	423.20	357	377	—0.2702
11.04	609.40	333	347	—0.2661
0.80	3.20	330	343	—0.2654

Exp. 15, VI. 1906. Emys orbicularis, Right nervus vagus. Non-polarising electrodes. Charging currents. Capac. 0.2 microfarad. Number of stimuli 10; (2 per second). Resting pauses between the series of stimuli 2 minutes. Experimental animal in 0.6% Na Cl solution, heated to 28° C.

Micro-coulombs	Ergs	First visible retardation noticeable in the second period of the stimulus in %	2nd idem in the 3rd period	Total retardation	$\sqrt[3]{}$ col. 3	$\sqrt[3]{}$ col. 4
0.48	5.76	13	139	224	—0.0785	—0.3889
0.496	6.15	20	99	155	—0.1111	—0.3334
0.504	6.35	20	139	205	—0.1111	—0.3889
0.52	6.76	26	152	224	—0.1404	—0.4035
0.552	7.61	26	152	224	—0.1404	—0.4035
0.616	9.48	26	152	218	—0.1404	—0.4035
0.744	13.83	28	199	270	—0.1587	—0.4762
1.116	31.13	21	157	270	—0.1261	—0.4579
5.58	155.65	28	157	284	—0.1587	—0.4579

Two particulars deserve notice:

1. that the greatest retardation falls not in the second but in the third period.

2. With stimulation with 7,61, 9,48, 13,83 ergs turbulent motions occur in the ventricle, followed by the post-undulatory pause, namely in the first systole after the preliminary retardation.

The relation brought to light in both these cases might be explained by assuming with LANGLEY that the vagus fibres do not reach the heart directly, but first pass a station of the intra-cardial ganglia. If this be the case the stimulated condition of the prae-ganglionic fibres will only be communicated to the post-ganglionic by contact in the ganglion cells. But then the quantitative coercion of WEBER's law holds for these ganglion cells and a relation as sketched above is not astonishing. To this conception may be objected that probably with stimulation of the post-ganglionic fibres (in the so-called n. coronarius [1]) the same relation will be found in its principal features. If on this point not only preliminary, but decisive experiments will have been made, it will be found that the just-mentioned explanation

[1]) On the n. coronarius as a post-ganglionic nerve vide J. GEWIN, l. c. 82.

is untenable. Mr. WOLTERSON accordingly gives an alternating explanation which, in my opinion possesses some probability, and which agrees with MARTIN's hypothesis on the nature of the vagus action.

Let us suppose that by the action of the vagus some catalytic substance — say MARTIN's K-ions — is produced in the receptive substance of the cardiac muscle, then the above stated quantitative relation will be explained, if we may assume that the substance, produced by vagus action, is only to a limited extent soluble in the medium. For with a small production of the catalyser this latter will be dissolved and will increase the retardation, but when the medium has become saturated with the catalyser, further secretion is without effect. It must further be assumed that the newly formed catalyser is at once removed from the substance by diffusion or is deposited in the form of indifferent compound, for the vagus action is known to cease after a short time. Only when the duration of the stimulus is increased and catalytic substance is again and again produced, the disappearance of the catalyser may be compensated and the retardation may be lasting.

The second chemical process we meet in Mr. WOLTERSON's thesis, that of the contractility, cannot be submitted to the above followed treatment, since the time-factor is wanting. We tried to introduce this latter by seeking the relation between the intensity of the vagus stimulation and the duration of the inotropic action, but this latter is not itself a chemical reaction, but only a modification of the conditions under which periodically recurring reactions take place. The negative inotropy may at the utmost be regarded as a diminution of the quantity C in the formula $\varphi = kC$, which amounts to the assumption that by vagus stimulation the quantity of the just mentioned substance, undergoing chemical change, is diminished. But this also is uncertain, for in the chemical reaction of the automatism C represents part of LANGLEY's receptive substance, which is different from the contractile substance. So I prefer to keep the two chemism apart and to consider the inotropy entirely by itself.

Placing ourselves on this point of view, we notice: 1. that with feeble and increasing vagus stimuli the inotropic effect on the sinus and auricle gradually increases with the intensity of the stimulus, until a certain degree of inotropy has been reached, after which it does not increase further for any intensity of the stimulus; 2. that an analogous relation holds good for the duration of the inotropic effect; 3. that the pessimum of contractility is found about the end of the first third or fourth part of the total duration, for which the inotropy exists.

Summarising we arrive at the following conclusions:

A. the chronotropy, produced by stimulation of the vagus, may be reduced to a negatively catalytic action on a chemical process which lies at the bottom of the pulsation.

B. the inotropy admits by analogy of a similar interpretation, but it is impossible to prove this, since at present no times of equal change can be determined here.

As secondary results we mention:

a. the existence of twofold negatively chronotropic fibres in the right vagus of the tortoise.

b. a particularly great sensitiveness of the heart of the tortoise for inotropy of the auricle by vagus stimulation, in such a degree that a single condensator discharge may produce the stated modification and that also with cumulative stimulation it appears sooner and lasts longer than the chronotropy.

c. the occasional occurrence of spontaneous cardiac turbulence in a warmed tortoise heart, immediately after a principal retardation brought about by vagus stimulation.

ERRATUM.

In the Proceedings of the meeting of December 29, 1906.

p. 504, line 13 from the bottom: for 2 read 4

p. 511, line 5 from the top: for 0.052 read 0.104

(February 21, 1907).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday February 23, 1907.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 23 Februari 1907, Dl. XV).

CONTENTS.

A. P. N. FRANCHIMONT: "Contribution to the knowledge of the action of absolute nitric acid on heterocyclic compounds" p. 600.

F. A. H. SCHREINEMAKERS: "On a tetracomponent system with two liquid phases", p. 607.

J. BOËSEKEN: "On catalytic reactions connected with the transformation of yellow phosphorus into the red modification". (Communicated by Prof. A. F. HOLLEMAN), p. 613.

J. D. VAN DER WAALS: "Contribution to the theory of binary mixtures", p. 621. (With one plate).

PH. KOHNSTAMM: "On the shape of the three-phase line solid-liquid-vapour for a binary mixture". (Communicated by Prof. J. D. VAN DER WAALS), p. 639.

PH. KOHNSTAMM: "On metastable and unstable equilibria solid-fluid". (Communicated by Prof. J. D. VAN DER WAALS), p 648. (With one plate).

W. H. KEESOM: "Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XIII. On the conditions for the sinking and again rising of a gas phase in the liquid phase for binary mixtures". (Continued). (Communicated by Prof. H. KAMERLINGH ONNES). p. 660.

H. KAMERLINGH ONNES and Miss T. C. JOLLES: "Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XIV. Graphical deduction of the results of KUENEN's experiments on mixtures of ethane and nitrous oxide", p. 664. (With 4 plates).

P. NIEUWENHUYSE: "On the origin of pulmonary anthracosis". (Communicated by Prof. C. H. H. SPRONCK), p. 673.

Chemistry. — "*Contribution to the knowledge of the action of absolute nitric acid on heterocyclic compounds.*" By Prof. A. P. N. FRANCHIMONT.

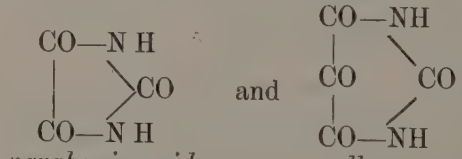
(Communicated in the meeting of January 26, 1907).

When searching about twenty years ago for the rules according to which nitric acid [1]) acts on hydrogen compounds, not only on those which contain the hydrogen in combination with carbon, but also on those which contain it in combination with nitrogen, I found that the hydrogen combined with nitrogen to the atomic group NH, does *not* act on nitric acid, when, in cyclic compounds, this group is placed between two groups of CO, but it *does* act if placed therein between the group CO and a saturated hydrocarbon residue [2]), and it may be added: *not* if placed therein between two saturated hydrocarbon residues, although I have not mentioned this previously.

It is a peculiar fact that the hydrogen of the group NH does not act on nitric acid if this group is placed between two similar groups such as CO, or saturated hydrocarbon residues, but it does act if placed between two dissimilar ones; so that it might be thought that a tautomeric form is essential for the reaction.

There are, therefore, in reality three rules, which, when considered more closely, apply also to acyclic compounds and which, although the cycle also exerts an influence, appear to spring mainly from the nature of the substance in which the group NH is placed: viz. secondary amine, amide or imide. In acyclic amides it was found that not only the acyl group in particular, but also the alkyl group exerts an influence on the reaction; we may, therefore, expect something similar in the cyclic ones.

The first of the above rules was mainly deduced from the behaviour of penta- and hexa-atomic cyclic urea derivatives, but was confirmed also in the case of other compounds. For instance

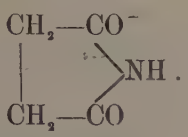


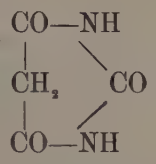
parabanic acid *alloxan*

[1]) Namely the real (absolute) acid which may be obtained by distilling a mixture of nitric acid 1.42 with twice its weight of sulphuric acid at a gentle heat under reduced pressure (Recueil XVI. p. 386).

[2]) Which, however, need *not* be the group CH_2 as stated wrongly by HARRIES (Annalen **327**. p. 358). The pages of the Recueil referred to by him contain exactly the proof of the contrary. I have also never spoken of "höchst concentrirter Salpetersäure" as he says, and of which he thinks he must "den Begriff festlegen", and for which he then recommends something which in many cases cannot give a good result.

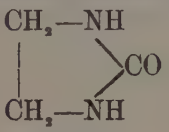
could be evaporated with nitric acid on a boiling waterbath without suffering any decomposition,

and also  *succinimide*

The  *malonureide*

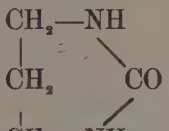
gives a nitroderivative, but with the nitro-group attached to the carbon; the two NH-groups do not act.

The second rule is also based mainly on the behaviour of penta- and hexa-atomic cyclic urea derivatives. For instance



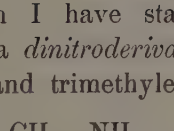
ethyleneureïne

gave a dinitroderivative, which on boiling with water yielded carbon dioxide and ethylenedinitramine. To this I may now add:

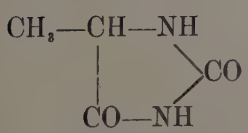


Trimethyleneureïne

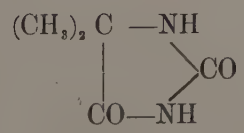
of which I have stated recently with Dr. FRIEDMANN that it gives directly a *dinitroderivative*, which on boiling with water yields carbon dioxide and trimethylenedinitramine.

 and its methyl derivatives

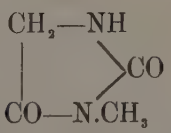
Hydantoin



α lactylurea



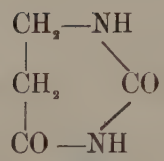
acetonylurea



1 *N*methylhydantoïn

gave mononitroderivatives, which on boiling with water were decomposed with evolution of 1 mol. of carbon dioxide and formation of a nitramino-amide; for instance nitrohydantoïn yields nitramino-acetamide.

To this I may add the

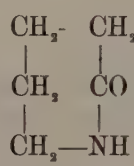


recently investigated with Dr.

hydro-uracil
(*β lactylurea*)

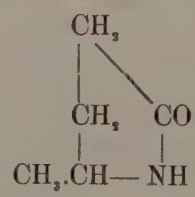
FRIEDMANN, which yields, equally readily, a *mononitroderivative*[1]), which on boiling with water yields, in an analogous manner, carbon dioxide and *β nitraminopropionamide*, from which we have prepared *β nitraminopropionic acid*, also its barium and silver salt.

This decomposition proves the position of the nitrogroup, and at the same time these substances are all a confirmation of the first rule because the group NH, which is placed between the two CO-groups, has not taken part in the reaction.



α Piperidone

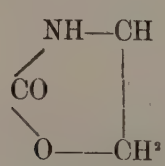
and



α methylpyrrolidone

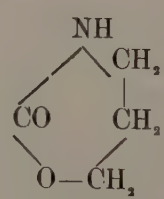
gave with nitric acid N_2O, presumably derived from a nitro-compound unstable towards nitric acid at the ordinary temperature; for it has been shown that some nitramides are decomposed by nitric acid at the ordinary temperature with evolution of nitrous oxide; whilst others may be evaporated with this acid on a boiling waterbath with impunity.

The rule was confirmed five years ago with cycles in which oxygen takes part, for instance



μ. céto tetrahydro-oxazole.

and



μ. céto pentoxazolidine

gave on evaporation with nitric acid, mononitroderivatives, which on

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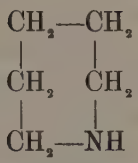
[1]) TAFEL stated about this substance (Ber. d. D. ch. G. 33 p. 3385) that it is not affected even by prolonged boiling with concentrated nitric acid; evidently he has not used absolute nitric acid.

boiling with water were decomposed with formation of carbon dioxide and a nitramino-alcohol.

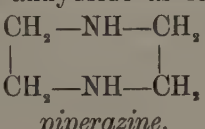
The third rule is derived from the behaviour of



piperidine

which yields with nitric acid a nitrate, but not directly a nitro-compound. This, however, may be prepared from a number of piperidides, to which we added recently the piperidides of *sulphuric* and *succinic acids*, or from the nitrate with acetic anhydride as found by BAMBERGER.

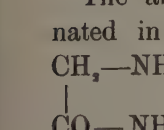
I have noticed recently that



piperazine.

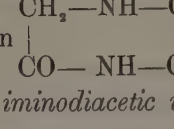
behaves in the same manner.

The above cited new investigations and those which follow originated in a research by Mr. A. DONK. He had prepared for practice



glycocol anhydride

and we treated this with nitric acid. But even on evaporation on a boiling waterbath it gave no evolution of nitrous oxide, no nitroderivative, but a nitrate. I had expected this behaviour sooner from the unknown



iminodiacetic imide

which is one of its isomeres, and in which one NH-group is placed between two CO-groups and the other between two saturated hydrocarbon residues, but not from glycocol anhydride in which each NH-group is placed between CO and a hydrocarbon residue, and about whose structure no doubt could be entertained. At most, we might suspect here a tautomer which does not react with nitric acid, or in all other cases in which nitric acid does act we might assume a tautomer and not here. [1])

Mr. DONK's nitrate, a very loose compound, appeared to be a mononitrate, and on applying BAMBERGER's method for amines (treatment

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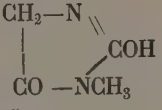
1) HARRIES l. c. suspects in 1 N methylhydantoïn a tautomer



which, however, yields with nitric acid the same nitromethylhydantoïn.

of the nitrate with acetic anhydride) he obtained a *mononitroderivative*, of which he proved the structure by acting on it with methyl-alcoholic potassium hydroxide, which yielded a properly crystallised acid, namely $NO_3\,NH\,CH_2\,CO\,NH\,CH_2\,CO_2\,H$.

nitraminoacetylaminoacetic acid

The reaction therefore took place as in all other cases where NO_2 and CO are both linked to a nitrogen atom; by absorbing the elements of water H and OH the group CO leaves the nitrogen whilst NO_2 remains attached to it.

After the departure of Mr. DONK, who did not wish to prosecute this matter, Dr. FRIEDMANN took it up and obtained the *dinitro-compound* from glycocol anhydride by treatment with excess of nitric acid and acetic anhydride. By the action of ammonia on dinitroglycocol anhydride nitroaminoacetamide was obtained, and by means of sodium hydroxide nitraminoacetic acid was formed in such a quantity that the formation of two molecules was no longer doubtful. The position of the two nitro-groups on the nitrogen atoms has, therefore been sufficiently proved.

CH_3-CH—NH—CO
| |
CO—NH—CH-CH_3

Alanine-anhydride

when evaporated with nitric acid also gave a nitrate only, which on treatment with acetic anhydride yielded a *dinitroalanine anhydride.*

These results, which formed a first deviation from the rule previously laid down, incited to further research. For it was shown plainly that besides the placing of the group NH between CO and a saturated hydrocarbon residue, the other part of the molecule may also influence the reaction in such a manner that a direct nitration is prevented, even on warming, although nitro-compounds actually exist.

The question, therefore, arose as to the behaviour of those isomers of glycocol anhydride, which possess the same atom-groups, but arranged in another order.

There may be eleven cyclic compounds which consist of two groups of NH, two groups of CO and two groups of CH_2, of whom however three only are described in the literature, namely:

CH_2—NH—CO
| |
CO —NH—CH_2

glycocol anhydride

CH_2—CH_2 CO
NH— CO—NH

hydro-uracil

and

CO—NH —CH_2
|
CO—NH—CH_2

ethyleneoxamide

The last one, however, only in an impure condition, as described by HOFFMANN in 1872, and which we have not yet succeeded in obtaining in a pure state.

This substance had a special importance. It has the two groups

NH, also between CO and CH_2, and, according to the rule, it ought to yield readily a dinitro-derivative; either stable or unstable. Still it might be that it was not attacked at all by absolute nitric acid, for if we remember that diacetamide, although slowly, still evolves N_2O with nitric acid and, therefore, presumably forms an unstable nitro-compound under those circumstances, and if we compare this with the cyclic succinimide, which is not attacked at all even on warming and which is connected with it in such a manner that it contains two hydrogen atoms less, and thus causes the cyclic combination, one feels inclined to attribute to the cyclic combination the prevention of the action of the nitric acid. We might also compare ethyleneoxamide to dimethyloxamide which is readily nitrated, and is related to it in the same manner as diacetamide to succinimide, and if the cycle formation has the same effect here as it has in the other case, ethyleneoxamide should not be attacked.

Preliminary experiments with the impure substance showed that no stable dinitro-derivate appears to be formed; at most, one which is at once decomposed by nitric acid, or it is not attacked at all. A very slow evolution of N_2O and CO_2 takes place, but this may be due to the impurity.

Of the eleven possible isomers there are only two urea derivatives namely hydro-uracil, which, as stated, conforms to the rule and gives a mononitroderivative. The second is $\begin{matrix} CH_2—CO—CH_2 \\ | \qquad\qquad | \\ NH—CO—NH \end{matrix}$. RÜGHEIMER

acetoneureïne

thought in 1892 that he had obtained this substance by the action of chloro-formic ester on diaminoacetone, but it was merely a surmise; no analysis was made and the properties were not investigated; and from our investigations it is extremely doubtful whether he had this substance in hand, for although we made the experiments in various ways we could obtain nothing else but *acetondiurethane*, from which a *dinitro-derivative* was readily obtained. A number of other methods for preparing acetonureine from diaminoacetone were tried but always without good result. In the meanwhile we are continuing our experiments for, we attach great importance to this substance as a second urea derivative, seeing that the first one conforms to the rule.

A fifth isomer would be $\begin{matrix} CO—CH_2—CO \\ | \qquad\qquad | \\ NH—CH_2—NH \end{matrix}$ which we have tried in

methylenemalonamide

vain to prepare from malonamide and formaldehyde. In this case it is the group CH_2 of the malonic acid which appears to react

principally; but even with the amide of dimethylmalonic acid and formaldehyde we have not arrived at the desired result. Methylenemalonamide is of importance for this reason, that the CH_2-group of malonic acid might give a nitroderivative, whilst this may be equally expected from the two NH-groups.

A sixth isomer is the already quoted $\begin{matrix} CH_2—NH—CH_2 \\ | \qquad\qquad | \\ CO—NH—CO \end{matrix}$ of which one might expect that it should yield with nitric acid only a nitrate, but not a nitro-derivative.

iminodiaceticimide

On heating the diamide of iminodiacetic acid in vacuo, Mr. JONGKEES obtained a substance which sublimes and has the composition of the imide. This, however, does not behave as was expected, but when evaporated with nitric acid, seems to give a nitro-derivative, whose properties are, however, somewhat different from the usual ones of nitramines or nitramides.

The last isomer of some significance for the problem under consideration, for the preparation of which no experiments have, as yet, been made, would be $\begin{matrix} CO—NH—CH_2 \\ | \qquad\qquad | \\ CO—CH_2—NH \end{matrix}$, in which one NH-group between CO and CH_2 renders probable a nitro-compound, whereas the second, placed between two CH_2, could only yield a nitrate.

The other four are derivatives of hydrazine, and are of no importance for our problem, because the two NH-groups contained therein are in a state of combination. One of those $\begin{matrix} CH_2—CO—NH \\ | \qquad\qquad | \\ CH_2—CO—NH \end{matrix}$ has been prepared by Dr. FRIEDMANN and, when it was brought in contact with nitric acid a violent evolution of red vapours was noticed, evidently caused by oxidation.

The details of these researches which of course, are being continued will appear in the "Recueil des Travaux chimiques des Pays-Bas."

But it is evident that the second rule will have to be altered, namely in that sense that the direct nitration (if any) of the heterocyclic compounds, which contain NH placed between CO and C_nH_{2n} depends also on the manner in which the groups, between which the group NH is placed, are combined; therefore it is the same as has been noticed with acyclic compounds. In how far the cycle itself plays a rôle has not yet been satisfactorily made out but we may point, provisionally, to one peculiarity, namely, that the three compounds which do not seem to conform to the previously established rule contain the NH-groups in the *para* position in regard to each other.

Chemistry. — *"On a tetracomponent system with two liquid phases."* By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of January 26, 1907).

Although in the systems of three components with two and three liquid phases there may occur many cases which have been predicted by theory, but have not yet been realised by experiment, I have still thought it would be as well to investigate a few systems with four components to have a glance at this as yet quite unknown, region.

I will now describe more fully a few of those systems built up from the substances: water, ethyl alcohol, lithium sulphate and ammonium sulphate.

We may represent the equilibria with the aid of a regular tetrahedron as in Fig. 1; the angular points represent the four components:

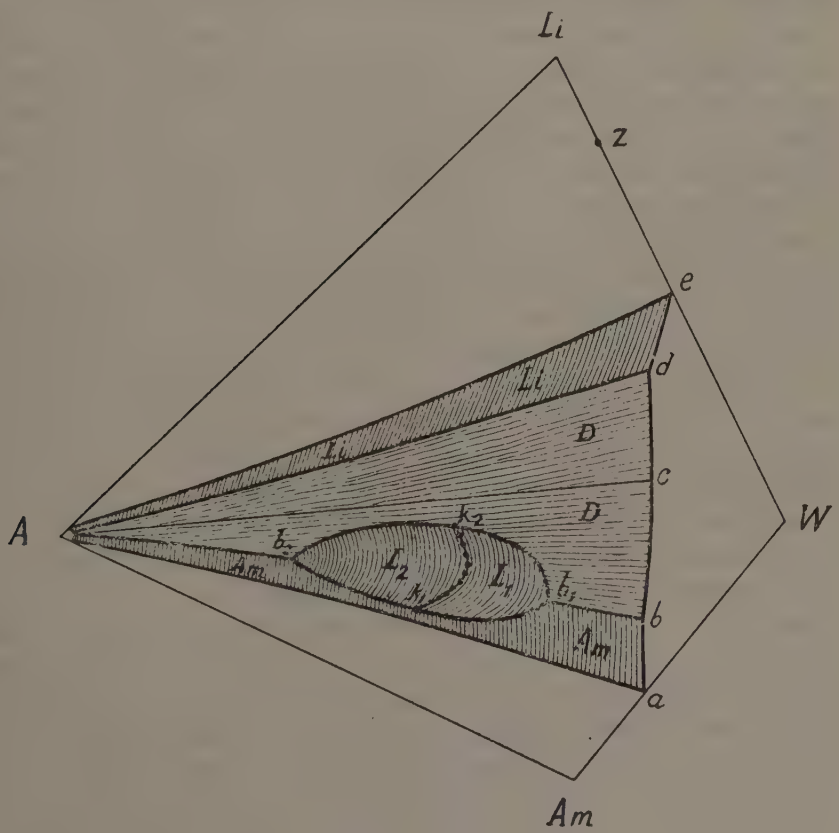


Fig. 1.

W = water, A = alcohol, Li = lithium sulphate, Am = Ammo-

nium sulphate. The side AW being invisible has been left out, also the side $Li\,Am$.

$Li_2SO_4 . H_2O$ and the double salt $LiNH_4SO_4$ may also occur as solid phases besides Li_2SO_4 and $(NH_4)_2SO_4$. The first is represented by a point Z on the side LiW, the second by a point D, not indicated, on the side $Li\,Am$.

The equilibria occurring at 6°5 are represented schematically by Fig. 1. The solubilities of the $(NH_4)_2SO_4$ and of the $Li_2SO_4 . H_2O$ in water are indicated by the points a and e; point c indicates the solubility in water of the double salt and must, therefore, be situated on the line WD (the point D is on the side $Li\,Am$). As Li_2SO_4, $(NH_4)_2SO_4$ and $LiNH_4SO_4$ are practically insoluble in alcohol, their solubility may be represented practically by the point A.

The curve aA is the saturation line of the $(NH_4)_2SO_4$; it indicates the aqueous-alcoholic solutions which are saturated with solid $(NH_4)_2SO_4$.

The aqueous-alcoholic solutions saturated with Li_2SO_4 and $Li_2SO.H_2O_1$ are represented by the curve eA which, however, must show a discontinuity in the immediate vicinity of the point A, for the curve consists of two branches, of which the one to the right indicates the solutions saturated with $Li_2SO_4 . H_2O$ and the one to the left those saturated with anhydrous Li_2SO_4.

The equilibria in the ternary system: water, lithium sulphate and ammonium sulphate are represented by the curves ab, bcd and de, which are situated in the side plane of the tetrahedron. ab is the saturation line of the ammonium sulphate, bcd that of the double salt $LiNH_4SO_4$, de that of $Li_2SO_4 . H_2O$. In my opinion, however, this latter is not quite correct, for, according to several analyses, Lithium sulphate seems to mix with the ammonium sulphate, although only to the extent of a few per cent, so that branch de indicates solutions saturated with mixed crystals. As, however, I have not accurately investigated this mixing, I will continue to speak in future of lithium sulphate monohydrate $Li_2SO_4 . H_2O$.

Let us now look at the equilibria in the quaternary system. The surface Am or $Aabb_1k_1b_2A$ represents solutions saturated with solid ammonium sulphate; surface D or $Ab_2k_2b_1bcdA$ represents the solutions saturated with $LiNH_4SO_4$; the curve Ac of this surface has as pecial significance, because it indicates the solubility of $LiNH_4SO_4$ in aqueous-alcoholic mixtures. The points of the surface D facing the curve Ac represent solutions which, in relation to the double salt, contain an excess of $(NH_4)_2SO_4$; the points behind this line show solutions containing an excess of Li_2SO_4.

The curve Ac must therefore, be situated in the plane passing through AW and the point D of the side $Li\,Am$. The surface Li or Ade indicates the liquid saturated with Li_2SO_4 or $Li_2SO_4H_2O$, or with the above mentioned mixed crystals; it must, therefore, consist of different parts which however, are not further indicated in the figure. At the temperature mentioned here (6°5) systems of two liquid phases may occur also; in the figure these are represented by the surface L_1L_2 or $b_1K_1b_2K_2$ which we may call the binodal surface; this binodal surface is divided by the line K_1K_2 into two parts L_1 and L_2 in such a manner that each point of L_1 is conjugated with a point of L_2. Two conjugated points indicate two solutions in equilibrium with each other: with each solution of the surface L_1 a definite solution of the surface L_2 may be in equilibrium.

Instead of a critical point, such as occurs with ternary mixtures at a constant temperature and pressure, a critical line is formed here, represented by K_1K_2. Each point of this line represents, therefore, a solution which is formed because in the system of two liquid phases $L_1 + L_2$ the two liquid phases become identical. Let us now look at the sections of the different surfaces: Ad then represents the solutions saturated with $LiNH_4SO_4$ as well as with $Li_2SO_4H_2O$; Ab_2 and b_1b indicate the liquids saturated with $LiNH_4SO_4$ and $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface Am namely, the curve $b_1K_1b_2$ indicates the system: $L_1 + L_2 + (NH_4)_2SO_4$ namely, two liquid phases saturated with solid ammonium sulphate. With each point of the curve b_1K_1 a point of b_2K_1 is conjugated. Each liquid of b_1K_1 may, therefore, be in equilibrium with a definite liquid of b_2K_1 while both are saturated with solid $(NH_4)_2SO_4$.

The intersection of the binodal surface with the surface D, namely, the curve $b_1k_2b_2$ represents the solutions of the system $L_1 + L_2 + Li\,NH_4SO_4$. With each liquid of b_1k_2 another one of b_2k_2 may, therefore, be in equilibrium while both are saturated with solid $Li\,NH_4SO_4$.

The points of intersection b_1 and b_2 of these two curves give the system: $L_1 + L_2 + (NH_4)_2SO_4 + Li\,NH_4SO_4$, namely two liquids both saturated with ammonium sulphate and lithium ammonium sulphate which may be in equilibrium with each other.

The points k_1 and k_2 have a special significance; both are critical liquids which, however, are distinguished from the other critical liquids of the critical curve k_1k_2 in that they are also saturated with a solid substance: k_1 is saturated with ammonium sulphate and k_2 with lithium ammonium sulphate.

If the temperature is raised the heterogeneous sphere is extended;

at about $\pm 8°$ the point k_1 arrives on the side $AWAm$, so that above this temperature a separation of water-alcohol-ammonium sulphate may occur in the ternary system.

I have further closely investigated at 30° the equilibria occurring in this quaternary system; the results are represented by the schematic figure 2.

The saturation surface Am which at 6°.5 still consists of a coherent whole, now consists (experimentally) of two parts separated from each other: this is because the binodal surface L_1L_2 now terminates on the side plane $AWAm$ in the curve $a_1k_1a_2$.

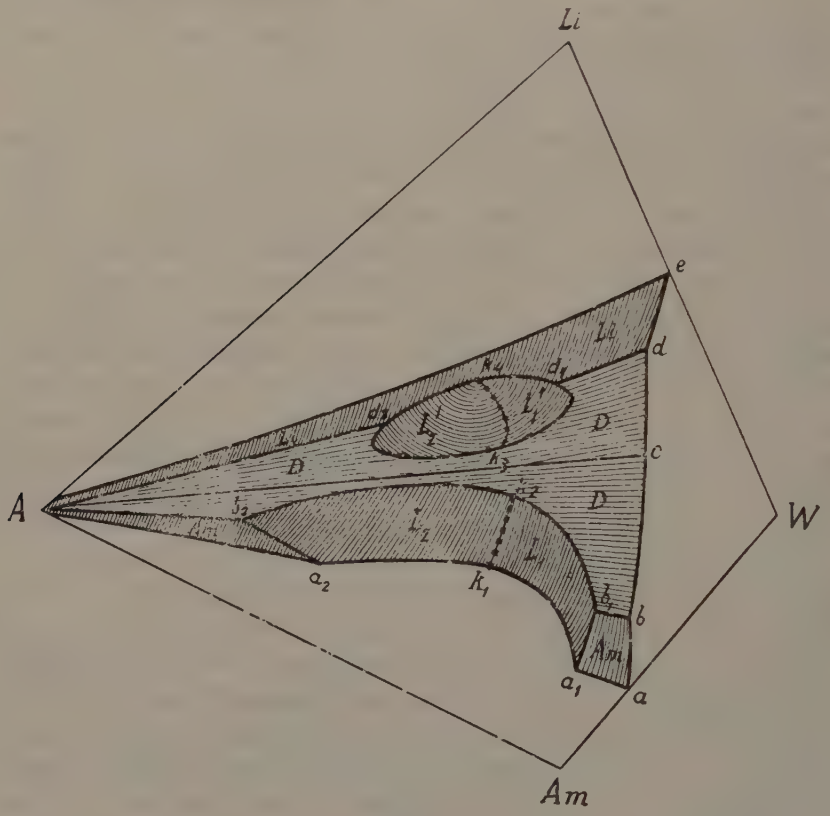


Fig. 2.

Of the critical line k_1k_2 the terminal point k_1 represents a ternary critical liquid; all other liquids of this line are quaternary critical ones, of which k_2 is saturated with solid lithium ammonium sulphate.

The phenomenon of the existence of a second heterogeneous region at this temperature was quite unexpected; it is represented in the figure by the binodal surface $L_1{}^1L_2{}^1$ or $d_1k_4d_2k_3$ with the critical line k_3k_4. I have not further investigated at what temperature this is formed; it is sure to be present at about 18°.

The binodal surface L_1L_2 intersects the saturation surfaces Am and D; we have, therefore, one series of two liquid phases, saturated with solid $(NH_4)_2SO_4$, and one series saturated with solid $LiNH_4SO_4$. The binodal surface $L_1^1L_2^1$ intersects the two saturation surfaces D and Li. We have, therefore, one series of two liquid phases saturated with $LiNH_4SO_4$ (curve k_3d_1 and k_3d_2), and one series saturated with $Li_2SO_4 . H_2O$ (curve k_4d_1 and k_4d_2). By d_1 and d_2 are represented two liquid phases which are in equilibrium with each other and saturated with $LiNH_4SO_4$ and $Li_2SO_4 . H_2O$. Of the series of the critical liquids represented by the curve k_3k_4, k_3 is saturated with $LiNH_4SO_4$ and k_4 with $Li_2SO_4 . H_2O$.

The curve Ac which indicates the liquids saturated with $LiNH_4SO_4$ without any excess of either of the components runs between the two heterogeneous regions. From this it follows that this double salt at 30° cannot give two liquid phases with water-alcohol mixtures.

We, therefore, have at 30° the following equilibria in the quaternary system.

liquids saturated with

1. $(NH_4)_2SO_4$, represented by the surface Am
2. $LiNH_4SO_4$, „ „ „ „ D
3. $Li_2SO_4H_2O$, „ „ „ „ Li
4. $(NH_4)_2SO_4$ and $LiNH_4SO_4$ „ „ the curves: bb_1 and b_2A
5. $Li_2SO_4H_2O$ and $LiNH_4SO_4$ „ „ „ „ dd_1 and d_2A

system of two liquid phases:

6. in itself represented by the surface L_1L_2
7. „ „ „ „ „ „ $L_1'L_2'$
8. saturated with $(NH_4)_2SO_4$, represented by the curves a_1b_1 and a_2b_2
9. „ „ $LiNH_4SO_4$, „ „ „ „ b_1K_2 and b_2K_2
10. „ „ $LiNH_4SO_4$, „ „ „ „ d_1K_3 and d_2K_3
11. „ „ $Li_2SO_4H_2O$, „ „ „ „ d_1K_4 and d_2K_4

two liquid phases saturated with:

12. $(NH_4)_2SO_4$ and $LiNH_4SO_4$, represented by the points: b_1 and b_2
13. $Li_2SO_4H_2O$ and $LiNH_4SO_4$, „ „ „ „ d_1 and d_2

critical liquids:

14. one series represented by the curve K_1K_2
15. „ „ „ „ „ „ K_3K_4
16. one critical liq. saturated with $LiNH_4SO_4$, represented by the point K_2
17. „ „ „ „ „ $LiNH_4SO_4$, „ „ „ „ K_3
18. „ „ „ „ „ $Li_2SO_4H_2O$, „ „ „ „ K_4

On raising the temperature over 30° the two heterogeneous regions gradually approach each other and finally unite; at what temperature this happens has not been determined, but from the experiments it is shown that this is already the case below 40°; I have also not been able to determine whether this point of confluence is situated in front or behind the curve *Ac*, or perhaps accidentally on the same.

I have closely investigated the equilibria occurring at 50° and represented the same by figure 3; any further explanation is super-

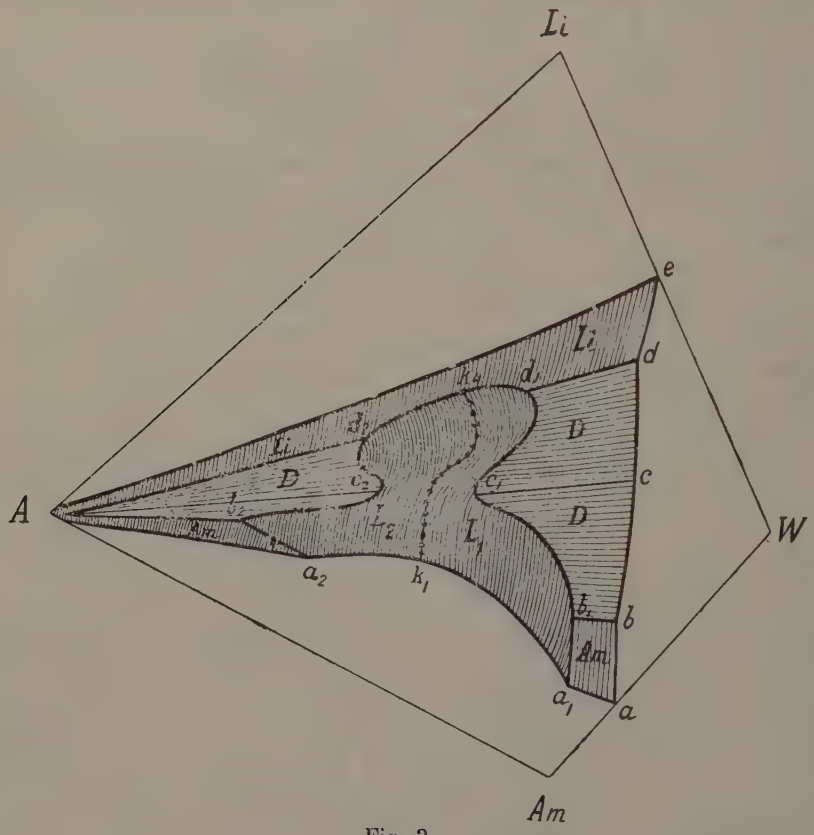


Fig. 3.

fluous. I must, however, say something as to the points c_1 and c_2, namely the intersecting points of the curve *Ac* with the saturating curve of the two liquid phases: b_1d_1 and b_2d_2. At first sight we might think that these two liquids may be in equilibrium with each other. That possibility, of course, exists. Suppose we take a water-alcohol mixture of such composition that two liquid phases occur on saturating with $LiNH_4SO_4$. Both liquids will now contain Li_2SO_4

and $(NH_4)_2SO_4$ and it is evident that two cases may occur. It may be that the two liquids contain the two components in the same proportion as they occur in the double salt; it is then as if the double salt dissolves in both liquids without decomposition. If this is the case the liquids c_1 and c_2 will be in equilibrium with each other.

The second possibility is that one of the liquids has in regard to the double salt an excess of Li_2SO_4 and the other, therefore, an excess of $(NH_4)_2SO_4$; in this case, c_1 and c_2 cannot be in equilibrium with each other. The experiment now shows such to be the case. When I saturated a water-alcohol mixture with $LiNH_4SO_4$ at 50°, the alcoholic layer contained a small excess of Li_2SO_4 and the aqueous layer a small excess of $(NH_4)_2SO_4$. From this it follows that the conjugation line does not coincide with the surface *DA W* but intersects it; the part to the right of the line must be situated in front of the plane and the left part behind it. The alcoholic solution c_2 of the double salt cannot, therefore, be in equilibrium with the aqueous solution c_1 of this double salt, but may be so with a solution containing an excess of $(NH_4)_2SO_4$.

Chemistry. "*On catalytic reactions connected with the transformation of yellow phosphorus into the red modification.*" By Dr. J. Böeseken. (Communicated by Prof. A. F. Holleman).

(Communicated in the meeting of January 26, 1907).

I.

From the researches of Hittorf (Pogg. Ann. 126 pag. 193) Lemoine (Ann. Ch. Ph. [4] 24. 129) Troost and Hautefeuille (Ann. Ch. Ph. [5] 2 pag. 153), R. Schenck (B. Ch. G. 1902 p. 351 and 1903 p. 970) and the treatises of Naumann (B. Ch. G. 187 2p. 646), Schaum (Lieb. Ann. 1898. 300 p. 221), Wegscheider and Kaufler (Cent. Blatt 1901 I p. 1035) and Roozeboom (Das heterogene Gleichgewicht I p. 171 and 177) it appears highly probable that red phosphorus is a polymer of the yellow variety, which polymerism is, however, restricted exclusively to the liquid and the solid conditions: the vapour (below 1000°) always consists of the monomer P_4.

From the above considerations it moreover follows that the yellow phosphorus is metastable at all temperatures below the melting point of the red phosphorus (630°); it may, therefore, be expected that it will endeavour to pass into the red variety below 630°.

Although there are many instances where a similar transformation, as with phosphorus at a low temperature, proceeds exceedingly slowly, the velocity in this case is certainly strikingly small. Even at 200°, when the metastable substance possesses a considerable vapour tension, it is still immeasurably small even though red phosphorus may be present. [1]) This extraordinary slowness, notwithstanding the considerable heat quantities liberated during the transformation, and the complete alteration of properties caused thereby, have a long time since established the conviction that the two modifications of phosphorus are each other's polymers and that the red one has a much more complex molecule than the yellow one, but the real cause of that slowness is not elucidated thereby.

As regards the question *how* this condensation takes place, SCHENCK (l.c.) was the first to endeavour to answer this experimentally. On boiling yellow phosphorus with an excess of PBr_3, he succeeded in changing it to the red modification at 172° with measurable velocity; and from his first investigations he concluded that the order of this reaction was a bimolecular one:

$$2\,P_4 \rightarrow P_8.$$

This was meant to represent the first phase, for SCHENCK pointed out that red phosphorus had no doubt a higher molecular weight than P_8, which subsequent condensation should then take place with great velocity; in other words he arrived at the rather improbable result that the condensation of P_8 to P_n would take place much more rapidly than that of the simple P_4 molecules to P_8.

At a repetition of these measurements with one of his pupils (E. BUCK), they came indeed to the conclusion that the reaction is monomolecular (B. Ch. G. 1903 p. 5208). He remarks "Daraus geht mit Sicherheit hervor, dass die Reaction der Umwandlung des weissen Phosphors in rothen monomolekular verläuft."

He, however, adds "Daraus könnte man den Schluss ziehen, dass die Molekular-gewichte des weissen und rothen Phosphors identisch sind."

It strikes me that SCHENCK arrives here at a less happy conclusion. From the occurrence of a mono-molecular reaction we need not necessarily come to the conclusion that the *entire* process proceeds in this manner.

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[1]) ROOZEBOOM (l.c.) compares this to the retardation of the crystallisation of strongly undercooled fusions as 200° is more than 400° below the melting point of red phosphorus: I am, however, of opinion that this view is untenable on account of the relatively high temperature, and particularly the very great mobility of the yellow phosphorus (ROOZEBOOM l.c. p. 89). The cause of the phenomena must be looked for elsewhere.

On the contrary as in so many other chemical transformations, we must assume that the measurements executed only apply to a subdivision of the reaction, namely to that with the smallest velocity.

In this case it is only natural to suppose that the velocity determinations of SCHENCK and BUCK apply to the decomposition of the P_4 molecule [1]) into more simple fragments (P_2 of P), then at once condense to the red modification so that we may represent the whole process in this manner for instance:

$$P_4 \text{ (yellow)} \rightarrow 2P_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$nP_2 \rightarrow P_{2n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which the reaction velocity of (2) is very much larger than that of (1).

(We might also suppose, as a primary reaction the transformation of the metastable phosphorus into a *labile* P_4; this, however, I do not think so probable because, in the determination of the vapour density above 1000°, a *splitting* has been indeed observed).

It cannot be a matter of surprise that this decomposition velocity at 200°, (without catalyst) will still be extremely small, looking at the great stability of P_4 in the state of vapour; and if this decomposition, as I suppose, must precede the condensation, the separation of the red phophorus at that temperature will proceed at least equally slowly.

There is also nothing very improbable in the very rapid transformation of the dissociated P_2 or P into red phosphorus.

The fact that the allotropic transformation takes place particularly under the influence of sunlight is certainly not in conflict with the idea of a primary splitting, as we know that the actinic rays accelerate the decompositions (such as of HJ, AgBr, C_2J_2, etc.).

I wish also to point out that a primary splitting is also accepted in other monomolecular reactions, such as in the decomposition of AsH_3 (VAN 'T HOFF's Vorlesungen), of CO (SCHENCK B. Ch. G. 1903 p. 1231 and SMITS and WOLFF. (These Proc. 1902 p. 417). [2])

The monomolecular splitting of C_2J_2 into C and C_2J_2 SCHENK and

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[1]) Although the size of the molecule of the liquid yellow phosphorus is not known with certainty, the identity with that of the vapour is however very probable; for the rest it does not affect the argument.

[2]) I omit purposely the beautiful researches of M. BODENSTEIN, although for the union of S and H. he also arrives at the conclusion that a primary splitting of the S_8 molecule precedes the union with H_2, because we are dealing here with heterogeneous systems in which solubility velocities play an important rôle. It is not impossible, that in all cases in which *amorphous* substances separate we are dealing with such solubility velocities.

SITZENDORFF B. 1905, p. 3459, may be interpreted in the simplest manner by the succession of the reactions:

$$C_2J_2 \rightarrow C + CJ_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$nC \rightarrow C_n \text{ and } 2\ CJ_2 \rightarrow C_2J_4 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

II.

The measurements of SCHENCK and BUCK have been made at the boiling point of PBr_3. As this is situated at 172°, it appears that the solvent exerts a considerable accelerating influence on the transformation, as pure yellow phosphorus at 200° remains practically unaltered.

The solvent, therefore, acts catalytically; a still more powerful influence has $AlCl_3$. If this is brought together with phosphorus in vacuum tubes, the transformation takes place even below 100°.

The catalyst is at once covered with a layer of pale red phosphorus, which it is rather difficult to remove by shaking, so that it is necessary to add now and then a fresh quantity of $AlCl_3$. The action proceeds much more regularly if benzene (and particularly PCl_3) is added as a solvent. At the boiling point of this, the transformation is completed after a few hours (respectively, minutes); the product is SCHENCK's scarlet-red phosphorus but much contaminated with benzene and condensation products, which are retained with great obstinacy.

In connection with the explanation in part I. I believe that the observations of SCHENCK and of myself throw some light on catalytic actions in general.

For it is very probable that in this allotropic transformation a splitting occurs first; we notice that the transformation, consequently the splitting, is accelerated by PBr_3 or $AlCl_3$. Will this not occur generally in catalysis? As a dissociation precedes most reactions it is probable that this question must be answered in the affirmative. (I wish, however, to lay stress on the fact, that in answering this question we do not penetrate into the real nature of catalysis. The reason *why* the dissociation acceleration occurs, whether this is connected with a temporary combination of the catalyst with the active molecules, or whether the catalyst removes the cause which impedes the dissociation, remains unexplained and need not be discussed here any further.)

As far as I have been able to ascertain, this conception is not antagonistic to the facts observed; in fact a number of cases are known where a catalyst causes *directly* a splitting or considerably accelerates the same.

Platinum, for instance, powerfully accelerates the decomposition of hydrogen peroxide, ozone, nitric acid, hydrazine etc.

Aluminium chloride causes a direct splitting of the homologues of benzene, of the very stable polyhalogen derivatives, of aromatic ethers, of sulphuryl chloride, etc. The number of these decompositions is so considerable that, in other cases where we cannot prove a direct dissociation by the catalyst, we may still argue that it takes place primarily, or rather that an already present but exceedingly small dissociation is accelerated in such a manner that a system attains the stable condition of equilibrium much sooner than without the catalyst.

The great evolution of heat in the process

$$HCCl_3 + 3\,C_6H_6 + (AlCl_3) = (C_6H_5)_3\,CH + 3\,HCl + (AlCl_3)$$

points to the fact that the system to the right is more stable than that to the left. I attribute its slow progress when no $AlCl_3$ is used to the small dissociation velocity of chloroform: the catalyst accelerates this dissociation so that the stable condition of equilibrium is attained in a short time. This reaction gets continuously more violent (the temperature being kept constant). This phenomenon may be readily explained if we bear in mind that the reaction proceeds in different stages ($C_6H_5\,CHCl_2$, $CHCl\,(C_6H_5)_2$ and $CH(C_6H_5)_3$ are formed in succession) and that the chlorinated intermediate products are decomposed much more readily than $CHCl_3$.

If sulphur is boiled with benzene and aluminium chloride we obtain almost exclusively $(C_6H_5)_2\,S$, $(C_6H_4)_2\,S_2$ and H_2S. Without the catalyst hardly any action takes place because the dissociation of S_8 in benzene solution at 80° is negligible: (if sulphur is boiled with toluene H_2S and condensation products are formed without $AlCl_3$ being present) the aluminium chloride accelerates the reaction $S_8 \rightarrow 4\,S_2$, and consequently the formation of the condensation products. This explanation is therefore quite the same as that given for the reaction of P_4 with benzene and aluminium chloride; the sole difference is that in the latter the second stage of the reaction consists exclusively in the condensation of P_2 to red phosphorus, a condensation to which sulphur does not seem to be liable to the same extent, so that the dissociated sulphur forms with benzene the above products.

I consider the formation of a compound of the catalyst with one of the reacting substances of importance for the taking place of the reaction in so far only that one phase can be formed; otherwise it rather obstructs the reaction, because the catalyst becomes to a certain extent paralysed. One of the most powerful catalysts, platinum, is actually characterised because it does *not* (or at least with great

difficulty) unite with the reacting molecules, but forms a kind of solid solution. Carbon tetrachloride which forms no compound with aluminium chloride is certainly attacked by benzene in presence of that catalyst not less easily than benzoyl chloride which does form an additive product; whilst also the chlorine atom in the acid chloride is certainly not less "mobile" than that of CCl_4.

GUSTAVSON imagines that the formation of compounds, such as $C_6H_3(C_2H_5)_3 Al_2Cl_6$ is necessary for the action of C_2H_5Cl on benzene; these were separated from the bottom liquid layer which forms during the action of C_2H_5Cl on benzene and aluminium chloride; if, however, the formation of this layer is prevented as much as possible, the yield of ethylated benzene improves. Therefore I do not call its formation *necessary*. That it may act favourably perhaps is because the catalyst and also the two reacting molecules are soluble in the same, thus allowing them to react on each other in concentrated solutions.

As has been observed above, there is something unsatisfactory in assuming intermediate reactions in order to explain catalytic phenomena. I will try to explain this matter more clearly.

As is known, we may express the reaction velocity of a condition change by the ratio: $\frac{\text{impelling force}}{\text{resistance}}$ in which the impelling force for that change in condition possesses a definite value which a catalyst cannot alter in the least; the resistance, however, is dependent on influences for the greater part unknown. Therefore, the resistance must be lessened by the catalyst and the question to be solved is: "On what does this decrease in resistance depend?"

If we suppose that intermediate reactions take place we divide the process into a series of others of which each one considered by itself is propelled by a force less impelling than the total change; the resistance of each of those division processes must, therefore, be much less, and the question then becomes: How is it that those intermediate reactions proceed much more rapidly than the main reaction? which is in fact nothing else but a circumlocution of the first question: how is it that the catalyst decreases the original resistance? Therefore, by assuming intermediate products, we have not been much enlightened, on the contrary we have made the problem more intricate, because, instead of having to account for a single increase of velocity, we have to look for that of at least two.

I call to mind the theory of OSTWALD who supposes each process to be a succession of condition changes, which will be all possible if they occur with potential diminution. If, however, the first of those

changes can commence only with absorption of free energy, the process will not take place unless a catalyst is added; this, therefore, opens another road . . . Now, in my opinion too much attention is paid to the milestones on that road and too little to the opening itself.

This is chiefly caused by the fact that we know so little of the so-called „passive resistances", for instance we cannot give a satisfactory explanation of the fact that iodine acts much more rapidly at low temperatures on metals than does oxygen, although the potential decline is much smaller. Still, I think that we must look for this mainly in the ready dissociation of the iodine molecule, always supposing that atoms react more rapidly than molecules, a supposition, moreover nearly a century old.

If this should be so, the action of a catalyst must be sought for in the increase of this dissociation.

Now, we know of a number of reactions where the catalyst forms undoubtedly a compound with one of the reacting molecules, which additive product then reacts with the second molecule to form the final product, with liberation of the catalyst, but even in such a case, which is called by many "pseudo-catalysis" (WAGNER, Z. Phys. Ch. 28 p. 48), I do not consider the *formation* of this compound as something essential without which the acceleration would not take place.

I certainly do not consider the formation of such an additive product as being without any significance, as it is an indication that the catalyst can exercise a particular influence on one of the molecules; the real increase of velocity is, in my opinion, due more to that influence than to the formation of the additive product, and in view of what precedes this, that influence consists presumably of an increase of the dissociation (and through this of the active mass).

It is, of course, obvious that a catalyst will act all the more energetically when the additive products are more labile. I have already mentioned platinum and now point also to the H-ions with which the formation of additive products, for instance when accelerating saponification, is far from probable. As a very lucid example, I mention the different catalytic influence which iodine and $AlCl_3$ exert on the transformation of yellow into red phosphorus.

From the researches of Brodie (Ann. de Ch. Ph. 1853 p. 592) which I have found fully confirmed, a small quantity of iodine can convert a large quantity of yellow phosphorus very rapidly into red phosphorus at 140°. (As in many other cases, there is a limit because the catalyst is precipitated by the colloidal phosphorus formed.

The velocity at the ordinary temperature is very small but becomes plainly perceptible at 80°. We are undoubtedly dealing here with a

case where the catalyst combines with the phosphorus to P_2I_4; this substance commences at 80° to dissociate measurably [so that its vapour density can only be determined at a low temperature (TROOST CR 95 293)] with separation of *red* phosphorus. We may, therefore give here a fairly positive answer to the question: How is it that the second division process proceeds more rapidly than the original? Because P_2I_4 dissociates much more rapidly than P_4.

But this is after all but a lucky circumstance, the real cause must be sought in the fact that in order to obtain P_2I_4 the P_4 molecule must be dissociated to begin with. With $AlCl_3$ I have not been able to find an additive product, only some indications that, besides the allotropic transformation, a trace of PCl_3 is formed (even with perfectly dry substances the manometer, after a few hours' heating to 100°, showed a slight increase of the vapour pressure).

The fact that the red phosphorus formed has in a high degree the property of coprecipitating the catalyst might perhaps indicate the possibility of a compound being formed between yellow phosphorus and $AlCl_3$; from the above it follows that there is a possibility of a certain reciprocal influence[1]) but I attribute this coprecipitation to the colloid properties of the red phosphorus, which, when obtained from solvents and also under the influence of rays of light, carries with it a certain quantity.

But even if an additive product is found, the existence of this substance is no more the cause of the acceleration than it is in the case of P_2I_4.

On the contrary, I consider the formation of a compound of the catalyst to be a case of "poisoning", caused by one of the reacting molecules, just as arsenic and prussic acid are poisons for platinum, because in combining with it, they prevent the entrance of O_2 and H_2 (respectively SO_2); just as ether is a poison for $AlCl_3$, because it unites with it to a firm compound, which does not decompose until over 100°, the temperature at which the catalyst again recovers itself.

Now, I cannot deny that we have not advanced much further with this dissociation theory (which is also not absolutely novel) for the question is now: How is it that a catalyst accelerates the dissociation? But my object was to point out that the formation (and eventually the admitting of the formation) of intermediate products can certainly never lead to an explanation of the catalytic phenomena.

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[1]) I have also found a similar reciprocal influence in the action of C_2H_5Br on $AlCl_3$ in which C_2H_5Cl and $AlBr_3$ are formed; it undoubtedly points to a dissociation.

Physics. — "*Contribution to the theory of binary mixtures.*" By Prof. J. D. VAN DER WAALS.

The theory of binary mixtures, as developed in the "Théorie moléculaire", has given rise to numerous experimental and theoretical investigations, which have undoubtedly greatly contributed to obtain a clearer insight into the phenomena which present themselves for the mixtures. Still, many questions have remained unanswered, and among them very important ones. Among these still unanswered questions I count that bearing on a classification of the different groups of ψ-surfaces. For some binary systems the plait of the ψ-surface has a simple shape. For others it is complex, or there exists a second plait. And nobody has as yet succeeded in pointing out the cause for those different forms, not even in bringing them in connection with other properties of the special groups of mixtures. It is true that in theory the equation of the spinodal curve which bounds the plait, has been given, and when this is known with perfect accuracy, it must be possible to analysis to make the classification. But the equation appears to be very complicated, and it is, especially for small volumes, only correct by approximation, on account of our imperfect knowledge of the equation of state. Led by this consideration I have tried to find a method of treatment of the theory which is easier to follow than the analytical one, and which, as the result proved, enables us to point out a cause for the different shape of the plaits, and which in general throws new light upon other already more or less known phenomena.

Theory teaches that for coexisting phases at given temperature three quantities viz. $-\left(\frac{d\psi}{dv}\right)_{xT}$, $\left(\frac{d\psi}{dx}\right)_{vT}$ and $\psi - v\left(\frac{d\psi}{dv}\right)_{xT} - x\left(\frac{d\psi}{dx}\right)_{vT}$ must be equal. The first of these quantities is the pressure, which we represent by p; the second is the difference of the molecular potentials or $M_2\mu_2 - M_1\mu_1$, which we shall by analogy represent by q. The third of these quantities is the molecular potential of the first component, which we shall represent by $M_1\mu_1$. Now the points for equal value of p lie on a curve which is continuously transformed with change of the value of p, so that, if we think all the p-curves to be drawn, the whole v,x-diagram is taken up by them. In the same way the points for given value of q lie on a curve which continuously changes its shape with change of the value of q; and again when all the q-lines have been drawn, the whole v,x-diagram is taken up. Both the p-lines and the q-lines have the property, that through a given point only one p-line, or only one

q-line can be drawn. One single p-line, however, intersects an infinite number of lines of the q-system, and every q-line an infinite number of lines of the p-system. One and the same p-line intersects a given q-line even in several points. However, it will, of course, be necessary, that if two points indicate coexisting phases, both the p-line and the q-line which passes through the first point, passes also through the second point. If we choose a p-line for two coexisting phases, not every arbitrarily chosen value for a q-line will satisfy the condition of coexistence in its intersections with the p-line, because a third condition must be satisfied, viz. that $M_1 \mu_1$ must have the same value. The result comes to this: when all the p-lines and all the q-lines have been drawn and provided with their indices there is one more rule required to determine the points which belong together as indicating coexisting points. So in the following pages I shall have to show, when this method for the determination of coexisting phases is followed: 1. What the shape of the p-lines is, and how this shape depends on the choice of the components. 2. What the shape of the q-lines is, and how this shape depends on the choice of the components. 3. What rule exists to find the pair or pairs of points representing coexisting phases from the infinite number of pairs of points which have the same value of q, when p has been given — or when on the other hand the value of q is chosen beforehand, to find the value of p required for coexistence.

But for the determination of the shape of the spinodal curve the application of the rule in question is not necessary. For this the drawing of the p- and the q-lines suffices. There is viz. a point of the spinodal curve wherever a p-line touches a q-line. We have viz. from $\frac{d^2\psi}{dv^2}\left(\frac{dv}{dx}\right)_p + \frac{d^2\psi}{dvdx} = 0$, and from $\frac{d^2\psi}{dxdv}\left(\frac{dv}{dx}\right)_q + \frac{d^2\psi}{dx^2} = 0$ for $\left(\frac{dv}{dx}\right)_p$ the value $-\frac{\frac{d^2\psi}{dxdv}}{\frac{d^2\psi}{dv^2}}$ and for $\left(\frac{dv}{dx}\right)_q$ the value $-\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dxdv}}$, and so we may write the equation of the spinodal curve:

$$\left(\frac{dv}{dx}\right)_p = \left(\frac{dv}{dx}\right)_q.$$

So if we are able to derive from the properties of the components of a mixture what the course of the p- and of the q-lines is, we can derive much, if not everything, about the shape of the spinodal curve. And even when the course of these lines can only be predicted qualitatively, and the quantitatively accurate knowledge is wanting,

the qnantitatively accurate shape of the spinodal curve will, indeed, not be known, but yet in large traits the reasons may be stated, why in many cases the shape of the plait is so simple as we are used to consider as the normal course, whereas in other cases the plait is more complex, and there are even cases that there is a second plait.

Particularly with regard to the p-lines, it is possible to forecast the course of these lines from the properties of the components. With regard to the q-lines this is not possible to the same extent, but if there is some uncertainty about them, we shall generally have to choose between but few possibilities.

THE COURSE OF THE p-LINES.

In fact the most essential features of the course of the p-lines were already published by me in "Ternary Systems" — and only little need be added to enable us to determine this course in any given case of two arbitrarily chosen components. As $p = -\frac{d\psi}{dv_{xT}}$ and $\left(\frac{dv}{dx}\right)_p = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$, it is required for indicating the course of these p-lines to know the course of the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$.

The former curve has a continuous liquid branch, and a continuous gas branch, at least when T lies below every possible T_k, when we denote by T_k the critical temperature for every mixture taken as homogeneous that occurs in the diagram. If there should be a minimum value of T_k for certain value of x, and T is higher than this minimum T_k, the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ has split up into two separate curves. In either of them the gas and the liquid branch have joined at a value of $v = v_k$. In this case a tangent may then be traced // to the v-axis to each of these two parts of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$.

The second curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ is one which has two asymptotes, and which may be roughly compared to one half of a hyperbola. The shape of this curve derived from the equation of state follows from the equation:

$$\frac{MRT\dfrac{db}{dx}}{(v-b)^2} - \frac{\dfrac{da}{dx}}{v^2} = 0.$$

If we now always take as second component that with the greatest value of b, so that $\frac{db}{dx}$ is always positive, it appears from the given equation that the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ cannot possess points for these values of x, for which $\frac{da}{dx}$ is negative. Only at that value of x for which $\frac{da}{dx} = 0$, this possibility begins, but then only if $T = 0$. If T has a definite value $\frac{da}{dx}$ must be positive, for points of this curve to be possible. For $v = \infty$, $\frac{da}{dx}$ must be $= MRT\frac{db}{dx}$. And the value of x which satisfies this equation, indicates one asymptote of the discussed curve by a line // to the v-axis. If this asymptote has been drawn, we may think the mixtures with decreasing critical temperature to be placed on its left side. And on the right the mixtures with increasing critical temperature do not yet immediately follow. For a separation between the mixtures with decreasing and those with increasing T_k, $\frac{da}{dx}$ must be $= \frac{a}{b}\frac{db}{dx}$; only when $MRT = \frac{a}{b}$ T_k would immediately ascend again on the right of this asymptote; but then T would have to be chosen so high, that it was $^{27}/_{8}$ T_k, and for the present at least we shall choose T far below that limit.

That the line $x = c$, where c has the value which follows from $\frac{da}{dx} = MRT\frac{db}{dx}$, is an asymptote, is seen when we think the equation of the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ written as follows: $\frac{v^2}{(v-b)^2} = \frac{\dfrac{da}{dx}}{MRT\dfrac{db}{dx}}$. As the value of $\frac{da}{dx}$ becomes larger from left to right, $\frac{v}{v-b}$ must increase from left to right, or $\frac{v}{b}$ decrease. For the value of x, following from $\frac{da}{dx} = MRT\frac{db}{dx}$, $\frac{v}{b}$ is infinite; for larger values of x, $\frac{v}{b}$ decreases

more and more, and as $\frac{v}{b}$ can never become $= 1$, because $\frac{da}{dx}$ cannot become infinite, the curve $v = b$ is the second asymptote. So if x is made to increase more and more, also beyond the values which for a given pair of components are possible in order to examine the circumstances which may occur with all possible systems for which with positive value of $\frac{db}{dx}$ increasing value of T_k is always found, a minimum volume must occur on the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$. So for this point $\left(\frac{d^2p}{dx^2}\right)_{vT} = 0$.

Now that we have described in general outlines the two curves which control the course of the p-lines, we shall have to show in what way they do so.

From

$$\left(\frac{dv}{dx}\right)_{pT} = -\frac{\left(\frac{dp}{dx}\right)_{vT}}{\left(\frac{dp}{dv}\right)_{xT}}$$

follows that to a p-line a tangent may be drawn // x-axis when it passes through the curve $\left(\frac{dp}{dx}\right)_{vT}$, and a tangent // v-axis, when it passes through the curve $\left(\frac{dp}{dv}\right)_{xT}$. But though these are important properties they would be inadequate for a determination of the course of the isobars, if not in general outlines the shape of one of these lines could be given. The line $\left(\frac{dp}{dx}\right)_{vT} = 0$ viz. intersects the line $\left(\frac{dp}{dv}\right)_{xT} = 0$ in two points, and it is these two points which are of fundamental significance for the course of the p-lines. The point of intersection with the liquid branch is viz. for a definite p-line a double point, the second point of intersection being such an isolated point that it may be considered as a p-curve that has contracted to a single point. The surface $p = f(x, v)$ is namely convex-concave in the neighbourhood of the first mentioned point. Seen from below a section // v-axis is convex, and a section // x-axis is concave. A plane, parallel to the v, x-plane touching the p-surface intersects, therefore, this surface in two real lines, according to which p has

the same value. But for the second point of intersection the two sections are concave seen from below — and there are no real lines of intersection. This second point is a real point of maximum pressure. With all these properties, and also with those mentioned before or still to be mentioned, $\frac{d^2a}{dx^2}$ is assumed to be positive. [1])

Now the curve $p =$ constant passing through the first point of intersection which the curves $\left(\frac{dp}{dv}\right)_{xT} = 0$ and $\left(\frac{dp}{dx}\right)_{vT} = 0$ have in common, is the isobar whose shape we can give, which shape at the same time is decisive for all those following, either for larger or smaller value of p. In the adjoined figure 1 its course is represented. Coming from the left it retains its direction to the right also in the point of intersection with the curve $\left(\frac{dp}{dx}\right)_v = 0$, the convex side all the time turned to the x-axis till it is directed straight downward in the point where it meets the vapour branch of the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$. There it has a tangent // v-axis, and from there it has turned its concave side to the x-axis. When it meets the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$, $\left(\frac{dv}{dx}\right)_p$ is equal to 0 for this as for all isobars. Passing again through the curve $\left(\frac{dp}{dv}\right)_{xT}, \left(\frac{dv}{dx}\right)_p$ is again infinitely large, and pursuing its course, it passes for the second time through the double point, and further moves to the right, always passing to smaller values of v, till it has again a tangent // to the axis of x, when it meets the curve $\left(\frac{dp}{dx}\right) = 0$ once more, after which it proceeds to larger value of v. It is clear that in the path it describes from the double point till it passes through this point for the second time, it has passed round the point we have called the second point

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[1]) That the characters of the two points of intersection of the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ are different appears among others from this that when these points of intersection coincide as is the case when these curves touch each other, the quantity $\frac{d^2p}{dv^2}\frac{d^2p}{dx^2} - \left(\frac{d^2p}{dx\,dv}\right)^2 = 0$. The character of the points of intersection depends on this quantity being positive or negative.

of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$, and where maximum pressure is found. In fig. 1 some more isobars have now been drawn besides this one. We obtain the course of the isobars for lower value of p by drawing a curve starting from the left at higher value of v, bearing in mind that two p-lines of different value of p can never intersect, because the p is univalent for given value of x and v. Such an isobar cuts the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$ on the left of the isobar with the double point in two points, where $\left(\frac{dv}{dx}\right)_{p} = \infty$, then passes through the curve $\left(\frac{dp}{dx}\right)_{vT} = 0$ in a point where $\left(\frac{dv}{dx}\right)_{pT} = 0$, and has then also on the right of the said isobar again two points of intersection with the curve $\left(\frac{dp}{dv}\right)_{xT} = 0$, in which points of intersection again $\left(\frac{dv}{dx}\right)_{pT} = \infty$.

An isobar of somewhat higher value of p has split up into two isolated branches. One of them starts on the right at somewhat smaller value of v; further this branch follows the course of the isobar with the loop, but must not cut it. Arrived in the neighbourhood of the double point it is always obliged to remain at small volumes; there it meets the curve $\left(\frac{dp}{dx}\right)_{v} = 0$, and it has $\left(\frac{dv}{dx}\right)_{p} = 0$. From this point it proceeds to smaller volumes, till a new meeting-point with the same curve causes this branch again to turn to larger volumes. But the second branch of this isobar of higher value of p is entirely inclosed within the loop of the loop-isobar. Such a branch forms a closed curve surrounding the point which we have called the second point of intersection of the curves $\left(\frac{dp}{dv}\right)_{x} = 0$ and $\left(\frac{dp}{dx}\right)_{v} = 0$. Such a closed branch passes twice through $\left(\frac{dp}{dx}\right)_{v} = 0$, and also twice through $\left(\frac{dp}{dv}\right)_{x} = 0$, and has again in the first cases $\left(\frac{dv}{dx}\right)_{p} = 0$, in the second points of intersection $\left(\frac{dv}{dx}\right)_{p} = \infty$.

With ascending value of p the detached portion of the p-line contracts more and more, till it has contracted to a single point. So at still higher value of p only one single branch of the p-line remains.

A similar remark must be made for the curves of lower value of p. The smallest value of p for gas volumes is of course $p = 0$; but this limit does not exist for the minimum pressure of the mixtures with given value of x. For this we know that also values of p may occur which are strongly negative. For values of p which are negative, the p-line has again divided into two disjointed portions, viz. a portion lying on the left in the diagram, which is restricted to volumes somewhat larger and somewhat smaller than that of the liquid branch of the curve $\left(\frac{dp}{dv}\right)_x = 0$, and a similar portion lying on the right in the diagram.

Also on the locus of the points of inflection of the isobars the given diagram can throw light. So it is evident in the first place, that between the two branches of the curve $\left(\frac{dp}{dv}\right)_x = 0$ starting from the double point, both on the left and on the right a connected series of points is found where $\left(\frac{d^2v}{dx^2}\right)_p = 0$. If the curve $\left(\frac{dp}{dv}\right)_x = 0$ itself should possess a double point, which is the case when T has exactly the value of T_k minimum, this locus of the points of inflection of the p-lines passes through this double point, and when the curve $\left(\frac{dp}{dv}\right)_x = 0$ has split up into two separate portions, as is the case for still higher value of T, then those points of the two portions where $\frac{dv}{dx} = \infty$ belong to this locus. It is also apparent from the diagram that two more series of points start from the double point, one on the right and one on the left, as locus of the points of inflection, and that these run to smaller volumes.

An isobar with somewhat larger value of p than that of the loop-shaped isobar has a tangent // to the x-axis where it passes through the curve $\left(\frac{dp}{dx}\right)_v = 0$. On the right and on the left of that point it turns its concave side to the x-axis, whereas at larger distance it must again turn its convex side to it on both sides. So there start from the double point four branches on which $\left(\frac{d^2v}{dx^2}\right)_p = 0$. It is also easy to see that the branch which moves to the right towards smaller volumes, must pass through that point of the curve $\left(\frac{dp}{dx}\right)_v = 0$ where the tangent is // x-axis. For an isobar which passes through

the curve $\left(\frac{dp}{dx}\right)_v = 0$ on the left of this point, turns its concave side to the x-axis, but when it passes for the second time through the said curve on the right of the point, its convex side. Hence an isobar where these two intersections have coincided, has its point of inflection in the point itself. If we wish to divide all the v,x-diagram into regions where $\left(\frac{d^2v}{dx^2}\right)_p$ is either positive or negative, it must be borne in mind that also the two branches of line $\left(\frac{dp}{dv}\right)_x = 0$ themselves form the boundaries for these regions, because on that line $\left(\frac{dv}{dx}\right)_p = \infty$.

In all this $\frac{d^2a}{dx^2}$ is supposed to be positive. For on the contrary the course of the line $\left(\frac{dp}{dx}\right)_v = 0$, to which we could now assign an existence on the right of the asymptote which is given by $MRT\frac{db}{dx} = \frac{da}{dx}$, would be directed to the left of this asymptote, when $\frac{d^2a}{dx^2}$ should be negative, so if $2a_{12}$ could be $> a_1 + a_2$. For as $\left(\frac{v}{v-b}\right)^2 = \frac{\frac{da}{dx}}{MRT\frac{db}{dx}}$, the value of $\frac{v}{b}$ decreases only, when $\frac{da}{dx}$ increases.

If we put $a = A + 2Bx + Cx^2$, and so $\frac{da}{dx} = 2(B + Cx)$, it appears that with C negative x must decrease in order to make $\frac{da}{dx}$ increase.

For the points of this line p would then possess a minimum for given value of v, and so $\frac{d^2p}{dx^2}_v$ would be positive. From this follows then that the two points of intersection of this line with the curve $\left(\frac{dp}{dv}\right)_x = 0$ have interchanged rôles. The point of intersection with the smallest volume represents then a real minimum of p, and will have the same significance for the course of the p-lines as the second point of intersection has, when $\frac{d^2a}{dx^2}$ is positive. And the point of intersection

with the smallest volume has now become double point. I have, however, omitted the drawing of this case 1. because most likely the case does not really occur, and 2. because the drawing may easily be found by reversing the preceding one. There are e.g. with the solution of salts in water cases which on a cursory examination present some resemblance with the assumption $\frac{d^2a}{dx^2}$ negative, but which yet are brought about by influences perfectly different from the fact of a negative value for $\frac{d^2a}{dx^2}$.

Such a diagram for the case $\frac{d^2a}{dx^2}$ negative, though, would quite fall in with the right side of fig. 1. As in the given figure T_k increases with x on the right side, and there is a maximum value of T_k on the supposition $\frac{d^2a}{dx^2}$, fig. 1 might be still extended to the right till such a maximum T_k was reached. But then we should also have to suppose that a value of x could exist or rather a mixture for which at a certain value of x the quantity $\frac{d^2a}{dx^2}$ reverses its sign.

Every region of fig. 1 of certain width which is taken parallel to the v-axis can now be cut out for $a_1 + a_2 - 2a_{12}$ positive, to denote the course of the isobars. Regions on the left side indicate the course of the isobars for mixtures for which with increasing value of b the critical temperature decreases — regions on the right side for mixtures for which with increasing value of b the critical temperature increases — the middle region with the complicated course of the isobars when there is a minimum T_k. The left region would be compressed to an exceedingly small one if we wished to exclude the case $\frac{da}{dx}$ negative or $\frac{da}{dx} = 0$. We do so when putting $a_{12} = \sqrt{a_1 a_2}$. On such a supposition a minimum T_k is still possible, but the left region must then have an exceedingly narrow width. There is, however, no reasonable ground for the supposition $a_1 a_2 = a_{12}^2$. There would be, if the quantity a for the different substances depended only on the molecular weights, and so $a = \varepsilon m^2$ held for constant value of ε. If the attraction, just as with NEWTON's attraction, is made to depend on the mass of the molecules, and so if we put $a_1 = \varepsilon_1 m_1^2$, and also $a_2 = \varepsilon_2 m_2^2$, it appears that ε_1 and ε_2 are not equal. If we now put $a_{12} = \sqrt{a_1 a_2}$, we put $a_{12} = m_1 m_2 \sqrt{\varepsilon_1 \varepsilon_2}$. What reasonable ground is there now for the sup-

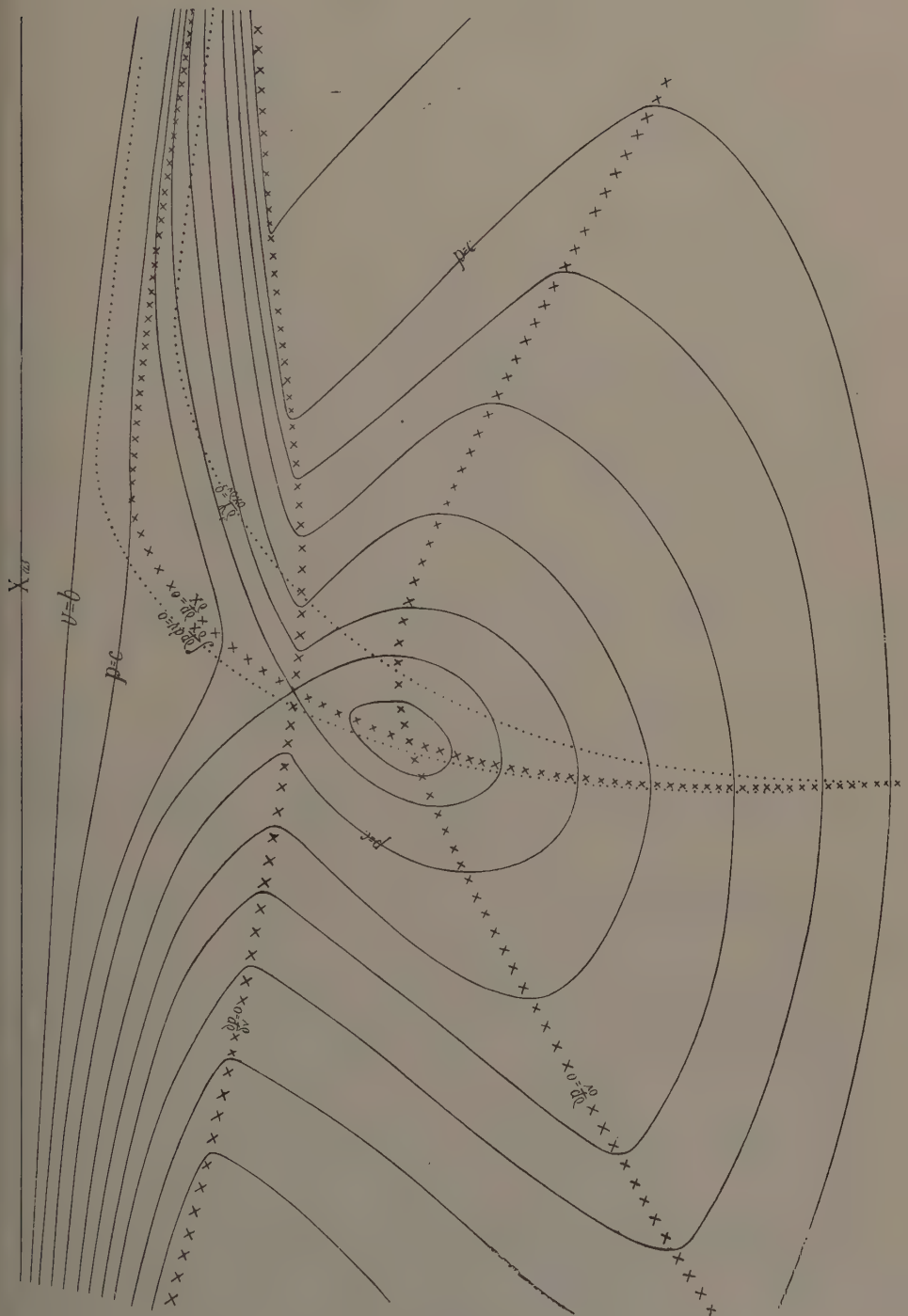

Fig 1.

position that if there is a specific factor ε_1 for the mutual attraction of the molecules of the first kind of which we do not know with what property of these molecules it is in connection, and if there is also a perfectly different factor ε_2 for the mutual attraction of the second substance, we must not represent the specific factor for the attraction of the different molecules inter se by ε_{12}, but by $\sqrt{\varepsilon_1\varepsilon_2}$. It is true that this supposition renders the calculations simpler; I had already drawn attention to this in my Théorie Moléculaire (Cont. II, p. 45). But whether the calculations are somewhat more or somewhat less easy does not seem a sufficient ground, after all, to introduce a supposition which involves that naturally a great number of possible cases, among others also for the course of the spinodal line, are excluded. If we put all possibilities for the value of a_{12}, then $\frac{da}{dx}$ can also be $=0$, viz. for $\frac{x}{1-x}=\frac{a_2-a_{12}}{a_1-a_{12}}$. We need not go so far however, to give sufficient width also to the left region.

THE COURSE OF THE q-LINES.

The value of $\left(\frac{d\psi}{dx}\right)_v=q$ is found from the value of ψ:

$$q=MRTl\frac{x}{1-x}+\int_v^\infty\left(\frac{dp}{dx}\right)_v dv.$$

For $x=0$ this expression is negatively infinite, for $x=1$ it is positively infinite, so that we have $q_0=-\infty$ and $q_1=+\infty$.

But it follows also from the equation of state that for all values of x the value of $\int_v^\infty\left(\frac{dp}{dx}\right)_v dv$ is also positively infinite for the line $v=b$. It is true that for such small volumes the equation of state $p=\frac{MRT}{v-b}-\frac{a}{v^2}$ is not accurate when b is not made to depend on v, and the quasi association in the liquid state is left out of account, and that the conclusion: $\int_v^\infty\left(\frac{dp}{dx}\right)_v dv$ is infinitely large for v equal to the limiting volume, calls for further consideration before we may accept this as an incontestable truth. But it seems to me that simple considerations lead to this conclusion. For the limiting volume p is infinitely great, and if b increases with x, $\left(\frac{dp}{dx}\right)_v$ is infinitely large

of higher order, whereas $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ can again diminish the order of infinity by a unit, because the factor of dv has this higher order of infinity only for an infinitesimal value of dv. But still the thesis remains true that $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv$ is infinitely great for $v = b$.

So there is strong asymmetry in the shape of the q-lines. Whereas $q = -\infty$ holds for $x = 0$ and every value of $v > b_1$, $q = +\infty$ holds all over the line of the limiting volumes, and for all volumes on the line $x = 1$ which are larger than b_2. We derive immediately from this, that all the q-lines without exception start from the point $x = 0$ and $v = b_1$. In this point the value of q is indefinite, as also follows from the value of q as it is given by the approximate equation of state, viz.:

$$q = MRT\, l \frac{x}{1-x} + MRT \frac{\frac{db}{dx}}{v-b} - \frac{\frac{dv}{dx}}{v}.$$

It also follows from the approximate equation of state that at their starting point all the q-lines touch the line $v = b$, of course with the exception of the line $q = -\infty$. For we derive from $\left(\frac{d\psi}{dx}\right)_v = q$

$$\left(\frac{d^2\psi}{dx\,dv}\right)\left(\frac{dv}{dx}\right)_q + \frac{d^2\psi}{dx^2} = 0$$

or

$$\left(\frac{dv}{dx}\right)_q = -\frac{\frac{d^2\psi}{dx^2}}{\frac{d^2\psi}{dx\,dv}}$$

For $\frac{d^2\psi}{dx^2}$ the approximate equation of state yields:

$$\frac{d^2\psi}{dx^2} = \frac{MRT}{x(1-x)} + \frac{MRT\frac{d^2b}{dx^2}}{v-b} + \frac{MRT\left(\frac{db}{dv}\right)^2}{(v-b)^2} - \frac{\frac{d^2a}{dx^2}}{v}.$$

We already found the value of $-\frac{d^2\psi}{dx\,dv} = \left(\frac{dp}{dx}\right)$ above. For $\left(\frac{dv}{dx}\right)_q$ we find therefore:

$$\frac{dv}{dx_q} = \frac{\dfrac{MRT}{x(1-x)} + \dfrac{MRT}{v-b}\dfrac{d^2b}{dx^2} + \dfrac{MRT\left(\dfrac{db}{dx}\right)^2}{(v-b)^2} - \dfrac{d^2a}{dx^2}}{v}}{\dfrac{MRT}{(v-b)^2}\dfrac{db}{dx} - \dfrac{da}{dx}\dfrac{1}{v^2}}$$

If we multiply numerator and denominator by $(v-b)^2$ and if we put $v=b$, we find for the starting point of the q-lines $\left(\frac{dv}{dx}\right)=\frac{db}{dx}$ at least if we can prove that $\frac{(v-b)^2}{x}$ is equal to zero for $x=0$ and $v=b_1$. To show this, we put $b=b_1+\beta x+\gamma x^2$, and so $v-b=$ $=(v-b_1)-x\beta-\gamma x^2$, and then we find for $(v-b)\ \frac{v-b}{x}$ the value:

$$(v-b)\left\{\frac{v-b_1}{x}-\beta-\gamma x\right\}.$$

The term $\frac{v-b_1}{x}$ is indefinite, but nevertheless the given value multiplied by $v-b$ is really equal to zero. This result, too, is still to be subjected to further consideration, because it has been obtained by the aid of the equation of state, which is only known by approximation. And then I must confess that I cannot give a conclusive proof for this thesis. But I have thought that I could accept it with great certainty, because in all such cases where a whole group of curves starts from one vertex of an angle, e. g. for the lines of distillation of a ternary system, I have found this thesis confirmed that then they all touch one side of the angle. Only in very exceptional cases the thesis is not valid.

Moreover, the theses which I shall give for the further course of the q-lines, are independent of the initial direction of these lines. Only, the q-lines themselves present a more natural course when their initial direction is the indicated one than in the opposite case.

From the value given above for $\left(\frac{dv}{dx}\right)_q$ follows that they have a tangent // v-axis, when $\left(\frac{dp}{dx}\right)_v=0$, and a tangent // x-axis, when $\frac{d^2\psi}{dx^2}=0$. Hence they have a very simple shape in a region where the lines $\left(\frac{dp}{dx}\right)_v=0$ and $\frac{d^2\psi}{dx^2}=0$ do not occur. Starting from the point $x=0$ and $v=b_1$ they always move to the right and towards

larger volume, and $\left(\frac{dv}{dx}\right)_q$ is always positive. Therefore $\left(\frac{dp}{dx}\right)_v$ and as will presently appear, $\frac{d^2\psi}{dx^2}$ are always positive in such a region. As v becomes greater the value of q approaches to $MRTl\ \frac{x}{1-x}$, and for very large value of v the q-lines may be considered as lines parallel to the v-axis, for which the distribution over the region from $x=0$ to $x=1$ is symmetrical. The lines for which q is negative, extend therefore from $x=0$ to $x=\frac{1}{2}$ and for $x=\frac{1}{2}$ the value of $q=0$. It will only appear later on that yet in their course probably two points of inflection always occur for small volumes, a fact to which my attention was first drawn by a remark of Dr. KOHNSTAMM, who had concluded to the presence of such points of inflection in the q-lines from perfectly different phenomena.

But as soon as the line $\left(\frac{dp}{dx}\right)_v=0$ is present (the case that also $\frac{d^2\psi}{dx^2}$ may be $=0$ will be discussed later on), a new particularity makes its appearance in the course of the q-lines. A q-line, viz., which cuts this locus, has a tangent $\parallel v$-axis in its point of intersection, and reverses its course in so far that further it does not proceed to higher value of x, but runs back to smaller value — so that $\left(\frac{dv}{dx}\right)_q$, which is always positive in the beginning, is henceforth negative. From that point where they intersect the line $\left(\frac{dp}{dx}\right)_v=0$ and where $\left(\frac{dv}{dx}\right)_q$ may be considered negatively infinite, this quantity becomes smaller negative. Still for $v=\infty$, the q-line must again run parallel v-axis. So there must again be a point of inflection in the course of the q-line. In fig. 2 this course of the q-lines has been represented, both in the former case when they do not intersect the curve $\left(\frac{dp}{dx}\right)_v$, and when they do so. In the latter case they have already proceeded to a higher value of x in their course than that they end in. They end asymptotical to a line $x=x_c$, and at much smaller volume they also pass through a point $x=x_c$. The point at which with smaller volume they have the same value of x as that with which they end, lies on a locus which has a shape presenting great resemblance with the line $\left(\frac{dp}{dx}\right)_v=0$. The value

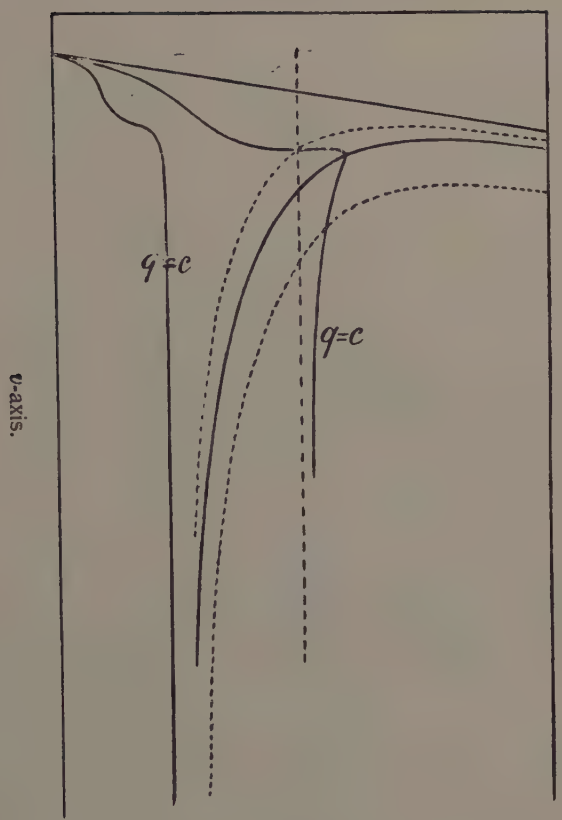

Fig. 2.

for the points of this locus may be derived in the following way.

If we write $\psi = MRT\{(1-x)\,log\,(1-x) + x\,log\,x\} + \int_v^\infty p dv$

then $\left(\frac{d\psi}{dx}\right)_v = q = MRTl\frac{x}{1-x} + \int_v^\infty \left(\frac{dp}{dx}\right)_v dv.$

At infinite volume the value of $q = MRTl\frac{x}{1-x}$ as we saw above. The locus under consideration must therefore be determined by $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$. Hence on the line $x =$ the final value, a point must

be found such that, proceeding along that same x-line, $\int_v^\infty \left(\frac{dp}{dx}\right)_v dx = 0$.

So from this follows immediately 1. that the points of the said locus restrict themselves to those values of x in which the curve $\left(\frac{dp}{dx}\right)_v = 0$ occurs, 2. that the points must be found with smaller volumes than those of $\left(\frac{dp}{dx}\right)_v = 0$. For such points with smaller volume is viz. $\left(\frac{dp}{dx}\right)_v$ positive, and for points with greater volume negative — however when the volume may be considered as a gas volume this negative value has an exceedingly small amount. And even without drawing up the equation $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$, we conclude that the said locus has the same x-asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and is further to be found at smaller volumes. Hence it will also have a point where its tangent runs // x-axis. There is even a whole series of loci to be given of more or less importance for our theory, which have a course analogous to that of $\left(\frac{dp}{dx}\right)_v = 0$ and $\int_v^\infty \left(\frac{dp}{dx}\right)_v dv = 0$.

The latter is obtained from $\left(\frac{dp}{dx}\right)_v$ by integration with respect to v; all the differential quotients with respect to v of the same function $\left(\frac{dp}{dx}\right)_v$ put equal to 0 have an analogous course — thus $\frac{d^2p}{dxdv} = 0$ which is a locus of great importance for our theory. That it has the same x asymptote as $\left(\frac{dp}{dx}\right)_v = 0$ itself, and that all its other points are to be found at higher value of v, follows immediately from the following consideration. For a point of the line $\left(\frac{dp}{dx}\right)_{vT} = 0$ the value of $\left(\frac{dp}{dx}\right) = 0$. For points of the same x and smaller v this value is positive — but for points with larger v negative. For $v = \infty$ this negative value has, however, again returned to 0. So there must have been a maximum negative value for a certain volume larger than that

for which this value $= 0$. These are the points for which $\frac{d^2p}{dxdv} = 0$. For smaller value of the volume $\frac{d^2p}{dxdv}$ is therefore negative — on the other hand positive for larger volumes. The approximate equation of state yields for the loci mentioned and for following loci these equations:

$$\frac{\frac{db}{dx}}{v-b} = \frac{\frac{da}{dx}}{v} \quad \text{for} \quad \int_v^\infty \frac{dp}{dx}\,dv = 0$$

$$\frac{\frac{db}{dx}}{(v-b)^2} = \frac{\frac{da}{dx}}{v^2} \quad \text{for} \quad \left(\frac{dp}{dx}\right)_v = 0$$

$$\frac{\frac{db}{dx}}{(v-b)^3} = \frac{\frac{da}{dx}}{v^3} \quad \text{for} \quad \left(\frac{d^2p}{dxdv}\right) = 0.$$

And so forth.

But let us now return after this digression to the description of the shape of the q-lines. Whenever a q-line passes through the locus $\int_v^\infty \left(\frac{dp}{dx}\right) dv = 0$, the asymptote to which it will draw near at infinite volume is known by the value of x for that point of intersection. For the present it does, indeed, pursue its course towards higher value of x, but when its meets the locus $\left(\frac{dp}{dx}\right)_v = 0$, it has the highest value of x, and a tangent $\parallel v$-axis. From there it runs back to smaller value of x.

And this would conclude the discussion of the complications in the shape of the q-lines, if in many cases for values of T at which the solid state has not yet made its appearance, there did not exist another locus, which can strongly modify the shape of the q-lines, and as we shall see later on, so strongly that three-phase-pressure may be the consequence of it.

The quantities $\frac{d^2\psi}{dv^2}$ and $\frac{d^2\psi}{dx^2}$ occur in the equation of the spinodal curve in the same way. It may be already derived from this that the existence of the loci $\frac{d^2\psi}{dv^2} = 0$ and $\frac{d^2\psi}{dx^2} = 0$ will have the same significance for the determination of the course of the spinodal line.

That as yet our attention has almost exclusively been directed to $\frac{d^2\psi}{dv^2} = 0$ is due to the fact that we know with certainty that a given binary mixture furnishes points for the latter locus for values of T below T_k for that mixture, whereas the conditions for the existence of a locus $\frac{d^2\psi}{dx^2} = 0$ are not known — and it might be suspected that this remained confined to temperatures so low that the solid state would have set in, and so the complications which would be caused by this, could not be observed. That such a supposition is not quite unfounded may still be safely concluded from the behaviour of many mixtures, which quite answer to the considerations in which the curve $\frac{d^2\psi}{dx^2}$ is left out of account. But that the behaviour of mixtures for which more complicated phenomena occur, cannot be accounted for but by taking into consideration that $\frac{d^2\psi}{dx^2}$ can be $= 0$, seems also beyond doubt to me.

The approximate equation of state gives for this quantity the following value:

$$\frac{d^2\psi}{dx^2} = \frac{MRT}{x\,(1-x)} + \frac{MRT\left(\frac{db}{dx}\right)^2}{(v-b)^2} + \frac{MRT\,\frac{d^2b}{dx^2}}{v-b} - \frac{\frac{d^2a}{dx^2}}{v}$$

which I shall still somewhat simplify by assuming that b depends linearly on x, and so $\frac{d^2b}{dx^2} = 0$. We can easily derive from this form that if $\frac{d^2\psi}{dx^2}$ can be $= 0$, this will be the case in a closed curve. At the boundaries of the v,x-diagram $\frac{d^2\psi}{dx^2}$ is certainly positive. For $x = 0$ and $x = 1$ even infinitely great. Also for $v = b$. And for $v = \infty$ it reduces to $\frac{MRT}{x\,(1-x)}$, the minimum value of which is equal to $4\,MRT$. That, if only T is taken low enough, it can be negative, at least if $\frac{d^2a}{dx^2}$ is positive, is also obvious. At exceedingly low value of T it can take up a pretty large part of the v,x-diagram, which must especially be sought in the region of the small volumes. With rise of temperature this locus contracts, and at a certain maximum temperature for its existence, it reduces to a single point. So it is no longer found above a certain temperature.

(*To be continued*).

Physics. *"On the shape of the three-phase-line solid-liquid-vapour for a binary mixture."* By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

Already for a considerable time I have been engaged in arranging Prof. VAN DER WAALS' thermodynamic lectures, and having arrived at the discussion of the three phase line solid-liquid-vapour, and the metastable and unstable equilibria solid-fluid which are in connection with it, I have formed on some points a different opinion from that laid down in the literature known to me on this subject. It does not seem unprofitable to me to shortly discuss the points of deviation in this and the following communication.

The first concerns the shape of the three phase line solid-liquid-vapour when the solid substance is one of the components, viz. the least volatile one. We find given for this that this line must always possess a pressure maximum [1]), and that it must also possess a temperature maximum [2]) when the solid substance, — as is usual, — melts with expansion of volume. The latter remark is the generalisation of a supposition, advanced by VAN DER WAALS [3]) with respect to the line for ether and anthraquinone. These considerations, however, hold only for definite assumptions on the extent of the difference of volatility of the two components. This appears immediately from the differential equation of the three phase line given by VAN DER WAALS [4]):

$$\frac{dp}{dT} = \frac{\eta_v - \eta_s - \frac{x_v}{x_l}(\eta_l - \eta_s)}{v_v - v_s - \frac{x_v}{x_l}(v_l - v_s)} \quad \ldots\ldots\ldots \quad (1)$$

in which η, x and v denote resp. entropy, concentration and volume of the coexisting phases, the index v, l and s denoting that resp. the vapour, liquid and solid phase is meant. x_s does not occur, because we assume, that the solid phase is the first component itself so $x_s = 0$. The pressure maximum will now occur in the line when the numerator, the temperature maximum when the denominator can become zero. Now $\eta_v - \eta_s > \eta_l - \eta_s$ and $v_v - v_s > v_l - v_s$; the two cases are therefore only possible when $x_v > x_l$, i.e. when the vapour is richer in the component which does not form the solid phase,

1) BAKHUIS ROOZEBOOM. Die heterogenen Gleichgewichte II. p. 331.
2) SMITS. These Proc. VIII, p. 196; Zeitsch. phys. Ch. LIV, p. 498.
3) These Proc. VI, p. 243.
4) Verslag Kon. Akademie V, p. 490.

(for in the equation is put $x_s = 0$) than the liquid. Or in other words, as we said above, the points sought can only present themselves in the three phase line with the least volatile component as solid substance[1]). However, whether those points *will* occur, depends on the value which $lim \left(\frac{x_v}{x_l}\right)_{x=0}$ will get. If this value may be put = infinite, we get for $x = 0$:

$$\frac{dp}{dT} = \frac{\eta_l - \eta_s}{v_l - v_s}$$

so equal to the slope of the melting-point curve. So we must have both pressure and temperature maximum, at least when the solid substance expands on melting. This was the purport of the above cited remark of VAN DER WAALS about ether and anthraquinone; if however $\left(\frac{x_v}{x_l}\right)_{x=0}$ may not be put infinite, this conclusion is no longer valid; it then depends on the value which:

$$v_v - v_s - \frac{x_v}{x_l}(v_l - v_s)$$

assumes for $x = 0$ whether there exists a temperature maximum or not; if the difference in volatility, so $\frac{x_v}{x_l}$, should not be so large, that this expression becomes negative at the limit, the maximum does not occur, even when $v_s > v_l$.

The question whether such a maximum will occur in many systems, cannot be answered with certainty for the present. For this many data would be required, which we have not at our disposal as yet; it is, however, possible to show the probability that only in very extreme cases the volability of the components will be so diversified, that a temperature maximum is to be expected. For this maximum to be just present, viz. in the triple point of the solid component, it is evidently required that:

$$\frac{x_v}{x_l} \frac{v_l - v_s}{v_v - v_s} = 1.$$

Now the first datum we should want, would be the variation of volume during melting. It seems, however, that only a few data have been collected for this; I have found some in WINKELMANN's "Hand-

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[1]) If has of course been tacitly assumed here, that there is no maximum vapour pressure; in that case the points in question could be found in *both* three phase lines.

buch" [1]), and in BAKHUIS ROOZEBOOM [2]); LANDOLT tables do not give anything on this subject. The values indicated at the places mentioned confirm that the percentage of these expansions is not very considerable, which was a priori to be expected; they amount for the highest cases to little more than 10% and for most substances they are considerably lower. So if we take 10% as basis, we shall find for by far the majority of the cases a too great, so for our proof a too unfavourable value. If we introduce this value, we get as condition (neglecting v_l by the side of v_v):

$$\frac{x_v}{x_l}\frac{v_l}{v_v} = 10.$$

So we must now try and get a rough estimation of the relation between liquid and vapour volume in the triple point. If at the triple point the vapour tension was of the order of an atmosphere, this ratio would be about of the order of magnitude 1000. Now, however, the vapour tension is always very considerably lower; almost for every substance the melting point lies very considerably below the boiling point. If we now assume that the triple point lies at about $^1/_2\, T_k$, we find the order of the vapour tension from the well known formula:

$$-\, l.\, nat \frac{p_c}{p_k} = f\left(\frac{T_k}{T} - 1\right).$$

With $f = 7$ and $T = {}^1/_2\, T_k$ this gives $log \frac{p_c}{p_k} = -7$ or $p_c = \frac{p_k}{1000}$.

If we put p_k at 100 atms.[3]), p_c becomes of the order of 0.1 atm. So we may safely say that in general v_l/v_v will be smaller than 0.0001. For a temperature maximum it is, therefore, necessary, that at least:

$$\frac{x_v}{x_l} = 10^6 \quad \text{or} \quad l.\, nat \frac{x_v}{x_l} = 11.5.$$

Now according to a formula which has been repeatedly derived by VAN DER WAALS [4]), for low temperatures (a condition which in this case is certainly fulfilled) the equation:

$$log. \frac{x_l}{1-x_l}\frac{1-x_v}{x_v} = \left(\frac{f}{m} - 1\right)\frac{dT_k}{T_k\, dx} + \frac{1}{b}\frac{db}{dx},$$

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[1]) II p. 612 2nd p. 775.

[2]) l. c. I p. 89.

[3]) In the table of LANDOLT and BÖRNSTEIN only two substances occur, ammoniac and water which have a higher p_k; the majority by far is considerably lower, particularly that of the little volatile substances which we have in view.

[4]) See e.g. These Proc. VII, p. 159.

holds, or for the limit, where $\frac{1-x_v}{1-x_l}=1$.

$$log.\frac{x}{x_v}=\left(\frac{f}{m}-1\right)\frac{dT_k}{T_k\,dx}+\frac{1}{b}\frac{db}{dx} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is clear that everything will depend on the first term here, because the second would not amount to more than -1 in the utmost case, i.e. when the b of the other component would be zero. Moreover it might even be possible that the second term was positive, it would hence decrease the value of the second member.

The greatest difficulty for our calculation lies now in our ignorance of with the variability of T_k with x, or more strictly in this that for this variability not one fixed rule is to be given, because in every special case it will depend on the special properties of the mixture in question, viz. on the quantity a_{12}, a quantity which does not admit of being expressed [1]) in the characteristic quantities of the components, at least for the present. It is, therefore, certainly not permissible to try and derive results for all kinds of systems. But it is only our purpose to determine the course of T_k for those cases, in which the components differ exceedingly much in volatility, and for those cases it is perhaps not too inaccurate a supposition to assume for the present that the line which represents T_k as function of x, does not deviate too much from a straight one. [2]) On this supposition then we may write $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ for $\frac{1}{T_k}\frac{dT_k}{dx}$. As now $\frac{f}{m}=14$, as we already supposed, $\frac{T_{k_2}-T_{k_1}}{T_{k_1}}$ must not descend considerably below

[1]) The equation of GALITZINE-BERTHELOT $a_{12}^2=a_1\,a_2$, which I rejected as general rule already on a former occasion on account of the properties of the mixture ether-choroform (These Proc. IV, p. 159), can certainly not be accepted as such. Not only is it easy to mention other examples which are incompatible with this rule (see e.g. QUINT, Thesis for the doctorate p. 44; GERRITS, Thesis for the doctorate, p. 68); but besides, — and perhaps this must be considered as a still more serious objection — by assuming this equation we wilfully break up the unity of the isopiestic figure (v. d. WAALS, Proc. of this meeting p. 627) by pronouncing its middle region on the left of the asymptote to be impossible, whereas the left and right regions are considered as real. For if $a_{12}=\sqrt{a_1 a_2}$ it is never possible that $da/dx=0$ for whatever system; and this takes exactly place in the middle region. I had overlooked this in the paper mentioned; Prof. VAN DER WAALS has since drawn my attention to it. The already mentioned system of QUINT gives an example of the occurrence of this case $\frac{da}{dx}=0$; a_{12} is there smaller than even the smallest of the two a's.

[2]) Cf. VAN DER WAALS, These Proc. VIII, p. 272.

0.9, that $log. \frac{x_v}{x_l}$ may not become smaller than the required value 11.5, or in other words, for the maximum in temperature to be reached, the critical temperature of one component must be about ten times as high as that of the other. A system, in which hydrogen occurs, will most likely show the temperature maximum when the other component has its critical point above 0° C., but already when the more volatile component is nitrogen or oxygen, we shall be more restricted in the choice of the other component. For then the latter must have its critical point at about 1000° C. resp. 1250° C. If ether were the more volatile component, this temperature would almost amount to 4500° C.

This conclusion is hardly affected when we put the temperature of the melting point not at $^1/_2$, but at $^1/_3$ of the critical temperature, as it really is for a number of substances whose critical temperature and melting temperature are known. It is true that this considerably increases the second member of equation (2), and so $\frac{x_v}{x_l}$, but in the same ratio $\frac{v_v}{v_l}$ increases too, so that the quotient remains about unchanged. This is most easily seen when the condition on which a temperature maximum occurs, is written:

$$\frac{x_l}{x_v}\frac{v_v}{v_l} < 0.1 \text{ or } log. \frac{x_l}{x_v} + log.\, v_v - log.\, v_l < log.\, 0.1.$$

Now for $log. \frac{x_l}{x_v}$ we may introduce the value from the equation[1]):

$$log. \frac{x_l}{1-x_l}\frac{1-x_v}{x_v} = \left(\frac{f}{T}\frac{dT_k}{dx} - \frac{1}{p_k}\frac{dp_k}{dx}\right),$$

and write for $log.\, v_v$:

$$log.\, v_v = log. \frac{MRT}{p_c} = log.\, MRT + f\left(\frac{T_k}{T} - 1\right) - log.\, p_k,$$

so that the condition becomes:

$$\frac{m}{f}\left\{1 + \frac{dT_k}{T_k dx}\right\} - \frac{1}{p_k}\frac{dp_k}{dx} - log.\, p_k - log.\, v_l - f + log.\, MRT < log.\, 0.1.$$

So an increase of T will only affect the first term and the term $log.\, MRT$, and the logarithmic change of the latter will certainly amount to less than the change of the former. This now increases when T becomes smaller, hence when at $T = {}^1/_2\, T_k$ the inequality

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[1]) These Proc. VII, p. 559.

is not satisfied, this will certainly not be the case for $T = {}^1/_3\, T_k$.

Still, it would be too hazardous to assert that it has now been incontestably proved that e.g. for the system ether-anthraquinone no temperature maximum *can* occur. For we have had to make use of the supposition that T_k depends linearly on x, and though this supposition may possess some degree of probability for critical temperatures that differ much, it is just with substances which — as ether and anthraquinone-lie closer together, that there is some ground for expecting a deviation from the straight line. Only very few experimental data are at our disposal. As such may e. g. be used the determinations on the increase of the plaitpoint temperature by addition of little volatile substances, made by SMITS, CENTNERSZWER and BÜCHNER. For by means of the formula given by VAN DER WAALS[1])

$$\frac{dT}{Tdx_0} = \frac{dT_k}{T_k dx} + \frac{49}{45}\left\{\frac{dT_k}{T_k dx} - \frac{1}{7}\frac{dp_k}{p_k dx}\right\}^2 \quad . \quad . \quad . \quad . \quad (3)$$

in which we need only pay regard to the principal terms (those with T_k), we may calculate the value of $\frac{dT_k}{T_k dx}$ from those directly measured. If we now calculate by the aid of the thus found value of $\frac{dT_k}{T_k dx}$ and the supposition of rectilinearity, T_{k_2}, i. e. the value of T_k for the admixed substance, we find the data collected in the following table. (P. 645).

From this appears that the values calculated in this way at least for some substances, and particularly for anthraquinone according to the determination by SMITS, are not inconsiderably lower than double the melting point temperature. It may, therefore, be considered highly probable that these lines are convex seen from below, and so the absolute value of $\frac{dT_k}{T_k dv}$ will be larger than might be expected from the supposition of rectilinearity. With our imperfect knowledge of the further course of the plaitpoint line, and hence à fortiori of the line for T_k an estimation as to this will, naturally, remain very uncertain; but yet it seems to me that something about this may be ascertained in the following way. We have on the side of the ether:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \left(\frac{da}{adx} - \frac{db}{bdx}\right)_{x=0},$$

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[1]) These Proc. VII, p. 272 and 296.

Second component	First component	Observer	T_k calculated	Double the melting-point temperature
Anthraquinone	Ether	SMITS	932°	1120°
„	SO_2	CENTNERSZWER	1032	1120
Resorcin	„	„	903	960
Camphor	„	„	790	900
Naphthaline	„	„	770	700
„	CO_2	BÜCHNER	640	700
Paradichloro benzene	„	„	670	650
Paradibromo benzene	„	„	690	720
Bromoform	„	„	640	560
Orthochloronitro benz.	„	„	760	610

BÜCHNER's values have been borrowed from his thesis for the doctorate (Amsterdam 1905); those of CENTNERSZWER from a table by VAN LAAR (These Proc. VIII, p. 151); that of SMITS has been calculated from his determination: plaitpoint at 203° and $x = 0.015$, (These Proc. VII, p. 179).

and so when introducing for a the quadratic and for b the linear function:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=0} = \frac{2a_{12} - 2a_1}{a_1} - \frac{b_2 - b_1}{b_1} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Now it will not be too hazardous an estimation, when — keeping in view that the formula for ether is $C_4H_{10}O$ and for anthraquinone $C_{14}H_8O_2$ —, we put the size of the anthraquinone molecule at about two or three times that of the ether molecule; so $b_2 = 2b_1$ à $3b_1$. If we introduce this value and the value of $\frac{dT_k}{T_k dx}$, calculated by the aid of equation (3), into equation (4), we obtain a value for a_{12}. Assuming that the value of T_k for anthraquinone is $2 \times 560° = 1120°$, we can find an a_2 from the ratio of the critical temperatures of ether and anthraquinone, and the a for ether; and with these quantities we can finally calculate the $\frac{dT_k}{T_k dx}$ on the anthraquinone side from:

$$\left(\frac{dT_k}{T_k dx}\right)_{x=1} = \frac{2a_2 - 2a_{12}}{a_2} - \frac{b_1 - b_2}{b_2}.$$

Starting from $b_2 = 2b_1$ we find in this way $\left(\frac{dT_k}{T_k dx}\right)_{x=1} = 0.66$; with $b_2 = 2.5 : 0.65$ and with $b_2 = 3\,b_1 : 0.64$. The error which we committed in our choice of b_2, will, therefore, bring about no considerable modification in the result; it would, indeed, be considerably modified if the critical point of anthraquinone should prove to lie considerably higher than 1120°. This is not in contradiction with our former remark that it is of little importance whether the reduced temperature is $^1/_2$ or $^1/_3$ at the triple point; for this we started from the supposition of the linear dependence, whereas here we have abandoned this supposition, and calculate this dependence from the experimental data. So according to the course of reasoning followed here the a_{12} is given by the experiment, and the smaller value of m would now result in a higher value of a_2 at given b_1, b_2 and a_{12}. If our estimation may be considered as not too inaccurate, we may conclude that the deviation from rectilinearity does increase the value of $\left(\frac{dT_k}{T_k dx}\right)_{x=1}$, but by no means in the degree which would be required to reach the critical value 0.9. (The value derived from the supposition of rectilinearity is 0,58).

Though the foregoing calculations teach us hardly anything positive, they fix first of all our attention on the great desirability of more data concerning the values of the quantities a and b of very little volatile substances; for it appears again that the whole behaviour of all the systems in which such substances appear, is controlled by these quantities, and it would exactly be of great importance for the theory of mixtures, if its results could be tested by such cases where the properties of the two components differ strongly. It is true that it will not be easy to determine the critical point of such substances in the usual way, but we should have gained already much if we could obtain an estimation of the critical temperature by calculation of the a and b from the deviations from the law of BOYLE in rarefied gas state, so still some hundreds of degrees below the critical point.

And further I think that after the foregoing I may be allowed to draw this conclusion, that the appearance of a temperature maximum in the three phase line, far from being the general case, will be confined to mixtures of very exceptional nature.

Much more frequently than a temperature maximum will a pressure maximum occur. It appears from equation (1) that this will always be the case, when the expression:

$$(\eta_v - \eta_s) - \frac{x_v}{x_l}(\eta_l - \eta_s)$$

may become negative. Now it is true that we cannot properly say that $\eta_v - \eta_s$ is a heat of sublimation and $\eta_l - \eta_s$ a latent heat of melting, because the η's do not refer to the same concentration, but we may say that $\eta_v - \eta_s$ is of the order of magnitude of a heat of sublimation, $\eta_l - \eta_s$ of the order of a latent heat of melting. Or in other words $\eta_v - \eta_s$ will be about 7 or 8 times $\eta_l - \eta_s$. So in all cases where $\left(\frac{x_v}{x_l}\right)_{x=0} < 7$ the pressure maximum in the three phase line will also fail. Here too the necessary data are wanting to ascertain whether there are many systems for which the $\frac{x_v}{x_l}$ at the triple point will descend to this amount. For, determinations of vapour tension or direct determinations of the required ratio have been nearly always carried out at considerably higher temperature [1]), and for the calculation by the aid of the just used formula the necessary data fail here too; besides, it would be doubtful whether the formula would be accurate enough, now that we have to deal with such small amounts. But — quite apart from the existence of mixtures with minimum vapour pressure — the existence of a system like ether-chloroform [2]) where on the chloroform side x_v becomes almost equal to x_l, already proves, that such systems exist.

In any case to the scheme for the possible course of the two three phase lines in a binary system plotted by BAKHUIS ROOZEBOOM in Fig. 108 of Vol. II of his "Heterogene Gleichgewichte", must be added types VII and VIII, characterized by a succession of sections,

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[1]) Particularly when we notice that the ratio of x_v and x_l would have to be calculated from the formula:

$$\frac{1}{p}\frac{dp}{dx_v} = \frac{x_v - x_l}{x_v(1-x_v)} \quad \text{or} \quad \frac{1}{p}\frac{dp}{dx_l} = \frac{x_v - x_l}{x_l(1-x_l)}$$

and the value obtained will, therefore, strongly vary in consequence of a change of temperature of some ten degrees, which have generally an enormous influence per cent on the pressure in the neighbourhood of the triple point.

[2]) KOHNSTAMM and VAN DALFSEN, These Proc. IV, p. 159. BAKHUIS ROOZEBOOM (l.c. I p. 41) deems it probable that also systems of gases with water and of water with many salts will show a similar shape. However, for such systems whose three phase line for the least volatile substance shows a pressure maximum, at least at temperatures that do not lie too far from the triple point, the shape of the p, x-line will have to deviate considerably from the line drawn there in Figs. 15 and 19, because from that shape would follow $x_v = x_l$.

denoted by 1 . 7 . 4 . 5 and 1 . 7 . 8 . 5 in ROOZEBOOM's nomenclature [1]). Type VII (see Fig. 1), is therefore distinguished from III in this that

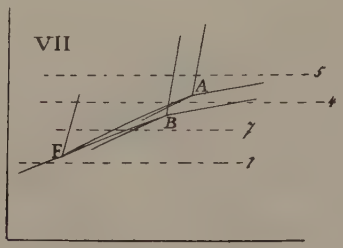

Fig. 1.

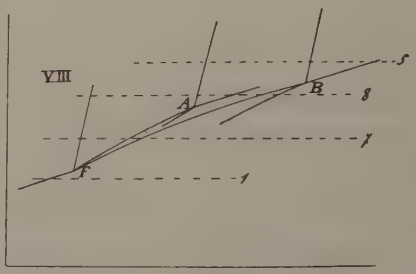

Fig. 2.

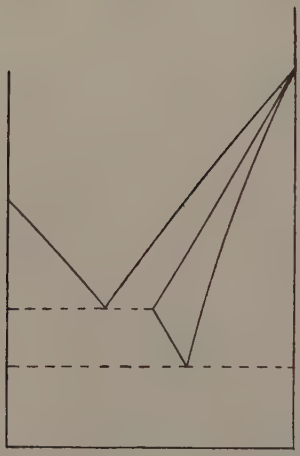

Fig. 3.

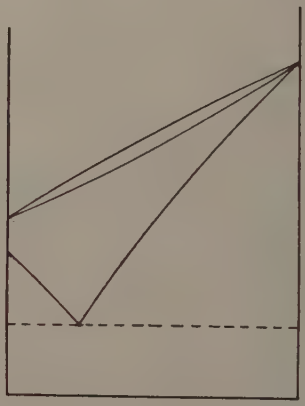

Fig. 4.

section 3 disappears; our Fig. 3 (lacking with ROOZEBOOM) takes its place. Type VIII (see Fig. 2) is distinguished from type V in this that instead of section 6 the section indicated in Fig. 4 appears between 8 and 5.

Physics. — "*On metastable and unstable equilibria solid-fluid.*" By Dr. PH. KOHNSTAMM. (Communicated by Prof. J. D. VAN DER WAALS.)

In a preceding communication [2]) I discussed a point on which I could not agree with the existing literature on the equilibria solid-fluid. A second point which will prove to be allied to the preceding one, concerns the course of the curves which are to indicate the

[1]) Loc. cit. p. 392.

[2]) Proceeding of this meeting, p. 639.

metastable and unstable equilibria solid-fluid in the T, x-figures drawn up by VAN DER WAALS [1]), and the v, x- and p, x-figures drawn up by SMITS [2]). VAN DER WAALS himself has already pointed out a defect in those figures [3]), viz. that the spinodal curve falls here within the connodal one, whereas in reality it falls far outside it at low temperatures; but it is not this that I have in view.

Let us first take the p, x-figures. According to them the complication which the binodal curve solid-fluid shows for temperatures below the triple-point, will disappear in this sense that at the triple point a *new complication* makes its appearance with three phase pressure, horizontal and vertical tangent, that then these two complications together give rise to the existence of a detached closed branch which contracts more and more, and at last disappears as isolated point. It is clear that in this way it is supposed that the complication can only disappear *above* the triple point, and not in the triple point itself, or in other words, that when the triple point is passed, always another three phase pressure is added to the existing one, and that these two more or less high, but always above the triple point pressure and the triple point temperature concur and disappear. Or expressed in another way still, it has been supposed in these figures that there is always found a temperature maximum in the three phase line. In the light of the considerations of our preceding communication this supposition is by no means legitimate. But apart from this there rise serious objections against these views. First of all, if these views are held, it is impossible to see what the shape of the binodal curve solid-fluid must be when the solid substance is the more volatile component. Moreover all through the succession of the p, x-figures the binodal curve solid-fluid has only one point in common with the axis $x = 0$. Now it is, however, known, that for the components themselves, so for the concentrations $x = 0$ and $x = 1$ the p, T-diagram of fig. 1 holds (see the plate), i. e. at the triple point temperature there exists by the side of the triple point pressure C a second pressure of equilibrium solid-fluid (viz. of an unstable phase) C', and above and below the triple point temperature these exist even two such pressures, one of which indicates metastable equilibrium, the other unstable equilibrium. But then the binodal curve solid-fluid for the mixture will not have to cut the axis of the component which becomes solid, once, but three times. And finally the p, x-figures of SMITS and the T, x-figures of VAN DER WAALS

1) These Proc. VIII p. 193.
2) These Proc. VIII p. 196.
3) loc. cit. p. 95.

cannot be made to harmonize with the v, x-figures plotted by the former; for in these threefold intersection of the binodal with the rim does really occur before the detachment takes place (Compare in fig. 6 of the said paper by SMITS the line fed with $f_1c_1e_1e_1'c_1'f_1'$; between this a v, x-line must necessarily be found intersecting the rim in three points). Now that attention has once been drawn to these unstable and metastable equilibria, it seems desirable to remove these discrepancies.

For this purpose the best thing is to start from the v, x-figure. The general equation of coexistence of phases in the variables v, x and T becomes in this case, if we now consider phase 2 as solid phase, 1 as fluid phase [1]):

$$(v_s - v_f)\left\{\frac{\partial^2\psi}{\partial v_f^2}dv_f + \frac{\partial^2\psi}{\partial v_f \partial x}dx_f\right\} + (x_s - x_f)\left\{\frac{\partial^2\psi}{\partial v_f \partial x_f}dv_f + \frac{\partial^2\psi}{\partial x_f^2}dx_f\right\} + \\ + \left(\frac{\varepsilon_{sf}}{T}\right)dT = 0,$$

so that we get for constant temperature:

$$\frac{dv}{dx} = -\frac{\frac{\partial^2\psi}{\partial v \partial x}(v_s - v_f) + \frac{\partial^2\psi}{\partial x^2}(x_s - x_f)}{\frac{\partial^2\psi}{\partial v^2}(v_s - v_f) + \frac{\partial^2\psi}{\partial v \partial x}(x_s - x_f)}.$$

In what follows we shall denote the numerator and the denominator of this fraction by N and D. The geometrical meaning of D has already been given by VAN DER WAALS in his first paper on these subjects [2]): the locus $D = 0$ is the locus of the points of contact on the tangents drawn from the point for the solid substance to the isobars. It is easily shown that the locus $N = 0$ is the locus obtained by putting the q-lines i.e. the lines $\frac{\partial\psi}{\partial x} = C$ in this instead of the p-lines. So a double point or an isolated point, as they are assumed by SMITS, can only occur where the loci $N = 0$ and $D = 0$ intersect. As in such a point, as appears from the geometric meaning, the p- and the q-lines have the same tangent, and accordingly touch, such a point must also lie on the spinodal line [3]). In perfect agreement

[1]) Cont.. II p. 104.

[2]) These Proc. VI p. 233.

[3]) For from the equation of the spinodal curve

$$\frac{\partial^2\psi}{\partial v^2}\frac{\partial^2\psi}{\partial x^2} - \left(\frac{\partial^2\psi}{\partial x \partial v}\right)^2 = 0 \text{ or } \frac{\frac{\partial^2\psi}{\partial v \partial x}}{\frac{\partial^2\psi}{\partial v^2}} = \frac{\frac{\partial^2\psi}{\partial x^2}}{\frac{\partial^2\psi}{\partial v \partial x}}$$

with this we easily obtain for the case that x_s is not 0 or 1, the course of the loci mentioned indicated in fig. 2. The dotted line denotes the concentration of the solid phase P; the lines $A\,Q\,B$ and $C\,Q'\,D$ are the two branches of the spinodal curve, the two other lines joining A with B and C with D the branches of $\left(\frac{\partial p}{\partial v}\right)_x = 0$. When now $x_s = 0$ becomes, it is evident that at this rim the line $D = 0$ must pass through the point where $\frac{\partial^2 \psi}{\partial v^2} = 0$, and this point coincides, as is known, with the spinodal curve at the rim. The conclusion seems obvious that the points Q and Q', the points of intersection of the spinodal curve and $D = 0$ have shifted towards the rim, and that, accordingly, the points of detachment and contraction from figs. 2—8 of Prof. SMITS (loc. cit.) would have to lie at the rim. However, this conclusion would not be correct. For the inference that where the spinodal curve and $D = 0$ intersect, on account of the geometrical meaning of $D = 0$ and $N = 0$, the latter must also intersect, does not hold good at the rim. This is in connection with $\frac{\partial^2 \psi}{\partial v^2}$ becoming zero and $\frac{\partial^2 \psi}{\partial x^2}$ becoming infinite. If we introduce the value MRT/x, which the last quantity for $x = 0$ gets, then N assumes the value:

$$\frac{\partial^2 \psi}{\partial v \partial x}(v_s - v_f) - x_f \frac{MRT}{x_f} = \left(\frac{\partial p}{\partial x}\right)_v (v_f - v_s) - MRT$$

and in general this expression will by no means be equal to zero in the points where $\left(\frac{\partial p}{\partial v}\right)_{x=0} = 0$, as already appears from the simple consideration that there can be no connection between $\frac{MRT}{v_f - v_s}$, a quantity which depends exclusively on the properties of the pure component and $\left(\frac{\partial p}{\partial x}\right)_v$ in the maximum and minimum points of its isotherm, because this latter quantity will also have to depend on the properties of the second component. So the points Q and Q' will certainly not lie at the rim, and in the points where $D = 0$

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follows:

$$-\left(\frac{dv}{dx}\right)_p = \frac{\left(\frac{dp}{dx}\right)_v}{\left(\frac{dp}{dv}\right)} = \frac{\frac{\partial^2 \psi}{\partial v \partial x}}{\frac{\partial^2 \psi}{\partial v^2}} = \frac{\frac{\partial^2 \psi}{\partial x^2}}{\frac{\partial^2 \psi}{\partial x \partial v}} = \frac{\left(\frac{\partial q}{\partial x}\right)_v}{\left(\frac{\partial q}{\partial v}\right)} = -\left(\frac{dv}{dx}\right)_q$$

cuts the rim the binodal curve will simply have a tangent parallel to the v-axis.

The shape which the different figures will assume, will now depend entirely on the fact whether such points Q and Q' will also exist when the solid substance is one of the components and if so, where they lie. The best and most general way of solving these questions would be a full consideration of the different forms which the q-lines may present. As however the solution of the special question we are dealing with does not call for such a discussion, I believed to be justified in preferring another briefer mode of reasoning. For this purpose I point out first of all that it is easy to see that at least in a special case such a point must exist also now. Let us imagine a plait, the plaitpoint of which has shifted so far to the side of the small volumes, that the tangent to the plait in the plaitpoint points towards the point indicating the solid state[1]). The plait touching the isobar in the plaitpoint, the plaitpoint lies evidently on the line $D = 0$ in this case[2]). But the plaitpoint lies also on the spinodal line, so the point Q lies here in the plaitpoint, as neither $\frac{\partial^2 \psi}{\partial v^2} = 0$, nor $\frac{\partial^2 \psi}{\partial x^2} = \infty$. We may conclude from this that in such like cases, so those cases where the plaitpoint has been displaced still somewhat further or somewhat less far to the side of the small volumes, and perhaps in general when the difference in volatility between the two components, is great, a branch of $N = 0$ will pass through the figure, and that it will most likely have a point of intersection with the line $D = 0$. A closer investigation of this supposition can, of course, only be given by the calculation.

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[1]) The above was written before Prof. ONNES' remarkable experiment (These Proc. VIII p. 459) had called attention to "barotropic" plaitpoints. Now that the investigations started by this experiment have furnished the proof that plaitpoints can exist, in which the tangent runs // x-axis, the existence of plaitpoints as assumed in the text, in which the slope of the tangent need not even be so very small, has, of course been a fortiori proved.

[2]) We may cursorily remark that it is therefore not correct to say in general that the line $D = 0$ runs round the plait in the sense which VAN DER WAALS (These Proc. VIII p. 361) evidently attaches to this expression, i. e. that the point of intersection of the line $D = 0$ with the binodal and spinodal curves would lie on either side of the plaitpoint. For if the plaitpoint should have moved still a little further to the side of the small volumes, the two points of intersection of $D = 0$ with binodal and spinodal curves lie evidently on the vapour branch of these lines (the part of these lines between the plaitpoint and the point with the largest volume on the x-axis).

For this we shall start with the case that b increases and a decreases with increasing x, so that T_k decreases strongly, and $\left(\frac{\partial p}{\partial x}\right)_v$ is positive everywhere; and for the present we confine ourselves only to the solidification of the least volatile component, so $x_s = 0$. Let us write the value which N gets at the rim by the aid of the value derived for $\left(\frac{\partial p}{\partial x}\right)_v$ from the equation of state, in the form:

$$(v_f - v_s)\left\{\frac{MRT}{(v-b)^2}\frac{db}{dx} - \frac{da/dx}{v^2}\right\} - MRT. \quad . \quad . \quad . \quad . \quad (1)$$

It is clear that this value will become negative for $v = \infty$, on the contrary positive for $v = b$ [1]); so there will always have to be a point on the axis $x = 0$, where $N = 0$. The value which N assumes for $x = 1$, is:

$$\left(\frac{\partial p}{\partial x}\right)_v (v_f - v_s) - \frac{MRT}{1-x}$$

and this expression will, accordingly, be negative for $x = 1$ for all possible liquid volumes, and even negative infinite. From this follows that from the point of intersection of $N = 0$ with the axis $x = 0$, the locus $N = 0$ will run to smaller volumes. Now whether $N = 0$ and $D = 0$ will intersect in our figure depends on the place where $N = 0$ cuts the axis $x = 0$. In this we may distinguish three cases:

1. The point of intersection of $N = 0$ and the axis lies at smaller volume than the points where $D = 0$ cuts the axis. Then no intersection of $N = 0$ and $D = 0$ will take place; the points Q and Q' lie quite outside the axes $x = 1$ and $x = 0$;

2. The point of intersection $N = 0$ with the axis lies between the points of intersection of $D = 0$ with it. Then the point of detachment does fall inside the figure, but not the point of contraction;

3. The point of intersection of $N = 0$ and the axis lies at larger

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[1]) If we should object to putting $v = b$, yet assuming that $v_f > v_s$, we shall in any case have to grant that there is nothing incompatible in the assumption that at a certain high pressure the volume in the solid state can be smaller than that in the liquid state, and that yet a great increase of pressure may be required to keep the substance in the same volume after we have replaced some of the molecules by much larger ones (so $\left(\frac{\partial p}{\partial x}\right)_v = \infty$).

[2]) As said, in every point of the line $N = 0$ the q-line passing through it, is directed to the point indicating the solid substance. Every q-line for infinite volume being $//$ v-axis, and terminating in the point $v = b$, it follows from the existence of the line $N = 0$ that every q-line cutting this locus, must at least possess one point of inflection.

volume. Then both the point of detachment and the point of contraction fall in the figure.

The consequences for the change of the v,x-projection of the binodal curve with variation of temperature will probably be clear from the figures 3—5 without further elucidation in these three cases. With regard to the frequency with which the three cases occur, it is evident that the last case will occur only rarely, with exceptionally high values of $\frac{db}{dx}$ and $-\frac{da}{dx}$, or in general of $\left(\frac{\partial p}{\partial x}\right)$. This case would be altogether impossible, if we had to take the temperature of the triple point, and the volume which the saturated vapour then has, into account, for this amounts certainly to some thousands of times b, and hence there will probably never be any question of an intersection of $N=0$ with the branch $D=0$ holding for the large volumes at the triple point temperature. But for our case we have not to reckon with this temperature, but with the highest temperature at which the binodal curve solid-fluid has still three points in common with the axis $x=0$, and this is evidently the temperature of point A in fig. 1. This, now, can probably lie very considerably above the triple point, and moreover — as we observed before — not the volume of the saturated vapour, but the much smaller one of the maximum of the isotherm must be introduced here. If we e. g. put the temperature of A so high that the maximum point of the isotherm lies at a volume $4b$, the expression will already become positive with $\frac{db}{dx}=3b_1$, or $b_2=4b_1$ and v_s near b, (da/dx is negative). So the case of 3 is, indeed, possible, but it also appears that it will occur only in exceptional cases [1]).

With none of these three cases do the T,x- and p,x-figures construed by VAN DER WAALS and SMITS, agree. They agree in so far with that mentioned under 3, that the point of detachment and the point of contraction are assumed to fall within the figure. But it is at the same time clear from the vx-figures, that a complication must begin

[1]) It appears from what has been said here that the figures 6—9 are meant quite schematically, for though we have drawn several binodals solid-fluid which hold for different temperatures, we have left the loci $N=0$ and $D=0$ unchanged. This has, of course, been done to save space, for else we could not have represented much more than one temperature in each figure without rendering the figures indistinct. But after what has been said it is clear that also the points Q and Q' move, and that it might e.g. very well happen that at lower temperatures the point Q' is not yet present in the figure, and that it makes its appearance only at higher temperatures. The following figures, too, are meant schematically, and serve only to elucidate the properties mentioned in the text.

in the p, x- and T, x-figures far below the triple point, viz. already at the temperature B of fig. 5, i. e. the temperature, at which in fig. 9 the new branch of the binodal curve (on the left side) makes its appearance in the figure. Let us first consider the p, x-lines.

At the temperature mentioned (T_1) a new branch begins to form at the same height as the spinodal line, so far below the point of the stable coexistence. In the p, x-figure the point where this appears, is, in opposition with the v, x-figure, indeed a point where the tangent is indefinite; for the equation:

$$N \,.\, dp = (x_s - x_f) \left\{ \frac{\partial^2 \psi}{\partial v_f^2} \frac{\partial^2 \psi}{\partial x_f^2} - \left(\frac{\partial^2 \psi}{\partial v_f \partial x_f} \right)^2 \right\} dx_f ,$$

holds for the former figure; the factor of dx_f is zero on the spinodal line and the factor of dp on the line $D=0$, which both pass through the point considered; so $\frac{dp}{dx}$ is there indefinite. The new branch extends more and more (fig. 6); its maximum continues to lie on the spinodal curve, and the point with the vertical tangent on the line $D=0$. When the temperature of detachment in the v, x-figure (T_2) has been reached, the old branch and the new one unite (fig. 7), and separate again as figure 8 represents. At the triple point temperature (T_3) the middle one and the topmost one of the three points of intersection with the axis coincide (in the final point of the double line vapour-liquid) (fig. 9); afterwards they exchange places. At still higher temperature the downmost point of intersection with the axis and that which has now become the middle one coincide; at this place there is again a point with indefinite tangent (T_4, the temperature A of fig. 1) (fig. 10); at still higher temperature the binodal curve solid-fluid has got quite detached from the axis, and its downmost branch forms a closed curve, which contracts more and more, and at last disappears at the temperature of the isolated point of fig. 5. Here it is evidently essential that T_4 lies above T_3, and T_3 above T_1, according to the significance which they have in fig. 1; also T_5, the point at which the detached branch disappears from the figure, must lie above T_3, the triple point, because in the triple point the binodal curve solid-liquid must still have two points in common with the rim (a little above it even three). But it is not essential that T_2 lies between T_3 and T_1; T_2 might just as well lie above T_3. Then we get the succession: fig. 6, fig. 9*a* (triple point), fig. 10*a*. If now T_2 lies below T_4, there is confluence and section, and we get after fig. 10*a* fig. 11, and then SMITS' figs. 4 and 5 (loc. cit); if T_2 lies also above T_4, first the two lowest points of intersection of the binodal curve d-

liquid with the rim join, then they are detached from the rim, and we get, therefore, in this case, but only above T_4, so above temperature A of fig. 1, the continuous line drawn by SMITS fig. 3 (loc. cit.), which then passes into figs 4 and 5 (loc. cit.).

The case mentioned under 2 that the point of contraction falls outside the figure may after all, be derived from the foregoing by putting T_5, the temperature at which the detached branch disappears from the figure, below T_4, the temperature at which it detaches itself from the rim. In our figures it has only this influence that the loop of figs. 9 and 10*a* cannot detach itself from the rim, as in fig. 10, and disappear as isolated point; but this loop contracts more and more at the rim and disappears there. In this case, too, T_2 can lie above T_3, but of course, not above T_4. If T_2 lies under T_3, we have the succession 6, 7, 8, 9 and disappearance of the loop in the rim; if T_2 lies above T_3 then: 6, 9*a*, 10*a*, 11, and disappearance of the loop in the rim.

The above case mentioned under 1, when also the point of detachment falls outside the v, x-figure, may be considered as the case that T_2 lies below T_1, and T_4 above T_5. We have then the succession, the upper portion of fig. 6 (viz. without the downmost loop), figs. 12, 8, 9, after which the loop merges in the rim. Now in all the cases mentioned, except in the second subdivision of the case under 3 (so T_2 above T_3), we meet still with two possibilities. Up to now we have assumed for those cases, that the triple point temperature is the highest temperature at which the two binodal curves intersect in the stable region, and that they have got detached above it. It is now, however, possible, that also in these cases the two binodals intersect twice at the triple point and above it. Then fig. 9*b*, is put everywhere for fig. 9, and then this is changed into fig. 11.

We get then the following summary:

Case under 1.

Upper portion of 6, 12, 8, 9,	disappearance of the loop in the rim
„ „ „ 6, 12, 8, 9*b*, 11	„ „ „ „ „ „ „

Case under 2.

6, 7, 8, 9,	„ „ „ „ „ „ „
6, 9*a*, 10*a*, 11	„ „ „ „ „ „ „
6, 7, 8, 9*b*, 11	„ „ „ „ „ „ „

Case under 3.

6, 7, 8, 9, 10,	disappearance of the loop in the fig.
6, 9*a*, 10*a*, 11, 4 and 5 SMITS	„ „ „ „ „ „ „
6, 9*a*, 10*a*, 3, 4 and 5 SMITS	„ „ „ „ „ „ „
6, 7, 8, 9*b*, 11, 4 and 5 SMITS	„ „ „ „ „ „ „

The greatest chance to only one intersection with the binodal curve liquid-vapour presents, of course, as is best seen from the v, x-figure, the case under 1, more particularly when in this case the line $N = 0$ cuts the axis at such small volumes, that it has no longer any point in common not only with the spinodal curve, but even with the binodal curve of the transverse plait. Only with a very exceptional course of the binodal curve of the transverse plait double intersection could take place in this case. On the other hand it will be highly probable that always when the line $N = 0$ cuts the binodal curve of the transverse plait (which will always have to take place in the cases under 2 and 3), also double intersection of the two binodals will be found.

This shows at the same time the connection of this investigation with that of the preceding communication. For it appears now that the shape of the p,x-lines holding for 1 with single intersection is, after all, by far the most frequently occurring, i. e. in almost all cases where no temperature maximum occurs in the three phase line; for in this case the triple point temperature is the highest temperature for which a three phase coexistence exists.

For a complete survey I have also indicated in figs 13—16, how the binodal curve for the other solid phase gets detached from the transverse plait. This is only possible in one way, because here there cannot be intersection of the lines $D = 0$ and $N = 0$. For $x = 1$ for this binodal curve, and so the expression for T' at the rim becomes:

$$\left(\frac{\partial p}{\partial x}\right)_v (v - v_s) + \frac{MRT}{x}$$

so always positive for both rims. The line $N = 0$ would therefore, have to become a closed curve, which on account of the shape of the q-lines may be considered as excluded [1]).

In the T,x-lines double intersection will, of course, always occur above the triple point when the three phase line has a maximum pressure. For the rest nothing of interest is to be said of the T,x-lines; they have the same general course as the p,x-lines given here, provided the figures are made to turn 180° round the x-axis, or in other words, provided a negative T-axis is made of the p-axis. Then the points with vertical tangent lie here, of course, on the line $W_{sj} = 0$, instead of on the locus $D = 0$; only at the rim they coin-

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[1]) At least as long as the complications, which are in connection with the existence of a locus $\frac{d^2\psi}{dx^2} = 0$, do not present themselves. (See v. d. waals, Proc. of this meeting p. 637). I shall perhaps revert later on to the changes which are to be made in what precedes in consequence of this.

cide. If the pressure maximum of the three phase line should be found at higher pressure than the point A of fig. 1, we must, of course, have the case mentioned under 3, i. e. the point of contraction must lie within the figure.

It has been assumed in the above that throughout the region $\left(\frac{\partial p}{\partial x}\right)_v$ = positive, and that a decreases with increasing b. The case that a increases with increasing b does not present any new points of view. If we have a system where a strongly increases, so that the critical temperature rises with b and $\left(\frac{\partial p}{\partial x}\right)_v$ is negative, the expression

$$(v - v_s)\left(\frac{\partial p}{\partial x}\right)_v + (x_s - x_f)\frac{MRT}{x_f(1-x_f)}$$

is evidently always negative for $x_s = 0$. And this is obvious, because this axis is now also that of the more volatile component; on the other hand the reversal of sign may now take place with the other axis. What happened on the left just now, will now take place on the right, and vice versa. It is only worthy of notice that now the line $N = 0$, if it exists, must intersect the axis $x = 1$ in two points. For the expression

$$(v - v_s)\left\{\frac{MRT}{(v-b)^2}\frac{db}{dx} - \frac{da/dx}{v^2}\right\} + MRT$$

where db/dx and da/dx are positive, becomes positive for $v = b$ and $v = \infty$. From this follows that besides the just mentioned cases, another possibility may be found, i. e. that the point of contraction does fall within the figure, but not the point of detachment. For the p, x- and T, x-figures it makes only this difference that a loop formed in the way of fig. 12, (which always disappeared in the rim in the other cases) may now also disappear like the loop of fig. 10 in a point within the figure. It is further clear, that in this case the point of contraction will much sooner fall within the figure than in the preceding case. For according to formula (1) $\frac{db}{dx}$ must have an excessively high value for the expression to be able still to become positive with a volume $v = 10\,b$. If, however, $da/dx = 2a_2 - 2a_{12} = 1.8\,a_2$ [1]), then:

[1]) With the values for a and b of LANDOLT and BÖRNSTEIN's table 82 we find about 12 for the highest value of $\frac{b_2}{b_1}$, about 250 for that of $\frac{a_2}{a_1}$; if hydrogen is excluded, the values become resp. 8 and 40. So, whereas with exclusion of hydrogen, pairs with a ratio $\frac{b_2-b_1}{b_1} > 7$ cannot occur, $\frac{a_2-a_1}{a_1}$ can reach the value 39.

$$\frac{da/dx}{v^2} = 1.8\,\frac{a}{v^2} = 1.8\left(\frac{MRT}{v-b} - p\right)$$

and so $(v-v_s)\,\frac{da/dx}{v^2}$ becomes of the order of magnitude $1.8\,\{MRT - p(v-v_s)\}$. With this volume and the low temperature holding here the latter term is certainly a small fraction of MRT, also $\frac{MRT}{v-b}\,\frac{db}{dx}$, so that the expression becomes negative.

Nor does the case that $\left(\frac{\partial p}{\partial x}\right)$ may become zero in the examined region, call for a further discussion, for it does not present any new points of view. If $\left(\frac{\partial p}{\partial x}\right)_v$ becomes zero in consequence of $\frac{da}{dx}$ first being negative then positive (minimum critical temperature), we shall have on either side what in the first case took place on the left side (fig. 6—12); if da/dx is first positive then negative (minimum of vapour pressure) we have on either side what happens on the right side in figs. 13—16.

Nor does, in view of the foregoing, the occurrence of cases in which the plaitpoint curve meets the three phase line, offer any difficulty. It is only clear, that the two points where this meeting takes place, must lie below the point of detachment (double point of the binodal curve solid-fluid) both in pressure and in temperature. For when detachment has taken place, and so the binodal curve has split up into two branches, it seems no longer possible, when the v,x-figure constantly contracts and hence $(\varepsilon_{sf})_v$ has a negative value, that the three phase pressure coincides with a plaitpoint pressure [1]). But nothing indeed pleads against this conclusion. Only when we cling to the supposition that the point of detachment must always lie at the rim we are confronted by unsurmountable difficulties. For then the temperature and pressure of the point of detachment coincide with those of B (fig. 1), and this point, lying considerably below the triple point, lies certainly, at least in pressure, far below any plaitpoint.

In conclusion we may remark that the cases where x_s lies between 1 and 0, i.e. where the solid substance is a compound entirely or partially dissociated in the fluid state, may be derived in all their details from the v, x-figure (fig. 2) without any further difficulty. We get then at low temperatures SMITS' diagrams in the figures 4—7 in his

1) Compare the figures referring to this in VAN DER WAALS, (These Proc. VI, p. 237, VIII, p. 194 fig. (2) and SMITS (These Proc. VI, p. 491 and 495 and VIII, p. 200 (fig. 10).

paper: Contibution to the knowledge of the p, x- and the p, T-lines [1], at least when we take the maxima of pressure very much higher and the minima very much lower, so that on the left side the figure intersects itself twice. The detachment of the two binodal curves then takes place in a very intricate way by means of a series of modifications, which I shall, however, omit, with a view to the available space. So, for this I must refer to the lectures which I am arranging for publication as mentioned in the beginning of my preceding communication, though certainly some time will elapse before they see the light.

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIII. *On the conditions for the sinking and again rising of a gas phase in the liquid phase for binary mixtures.* (continued). By Dr. W. H. KEESOM. Communication N°. 96^c from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 26, 1907).

§ 6. *Conditions for the occurrence of barotropic plaitpoints for mixtures with* $M_2 = 2\,M_1$, $v_{k_1} = 8\,v_{k_2}$. Now that it had appeared in § 5 (These Proc. p. 510), that there exists a barotropic plaitpoint [2]) on the assumptions mentioned there, first of all the occurrence of barotropic plaitpoints with $M_2/M_1 = 2$, $v_{k_2}/v_{k_1} = {}^1/_8$ was subjected to a closer investigation, partly also on account of the importance of these considerations for mixtures of He and H_2 [3]). The barotropic plaitpoints given in table I respectively for the ratio of the critical

[1]) These Proc. VIII, p. 200.

[2]) The proof that this barotropic plaitpoint really lies on the gas-liquid plait, is in connection with the discussion of the longitudinal plait. In a following Comm. by Prof. KAMERLINGH ONNES and me on this latter subject, the treatment of which was postponed for the present as stated in Comm. N°. 96b, the proof in question will be included.

[3]) To enable us to judge in how far this last assumption is in accordance with what is known about mixtures of He and H_2, the following remark may follow here, in the name of Prof. KAMERLINGH ONNES too, (cf. Comm. N°. 96b § 4, Dec. '06 p. 506) on b (cf. VAN DER WAALS, These Proc. Jan. '07, p. 528) and a for helium: It proved in the preliminary experiment described in Comm. N°. 96a that on analysis the liquid phase contained at least (some He has evaporated from it during the drawing off of the liquid phase) about 3 % He, the gas phase at least (a very small quantity of liquid has been drawn along with the gas phase being blown off) about 21 % H_2 (estimations of the corrections which for the reasons mentioned ought to be applied to the results of the analysis make it probable that they will not considerably influence the results derived here [added in the English translation]). Let us put the density of liquid hydrogen boiling under

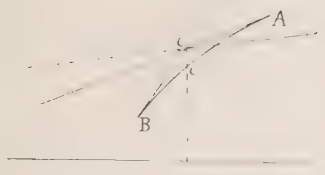

Fig. 1.

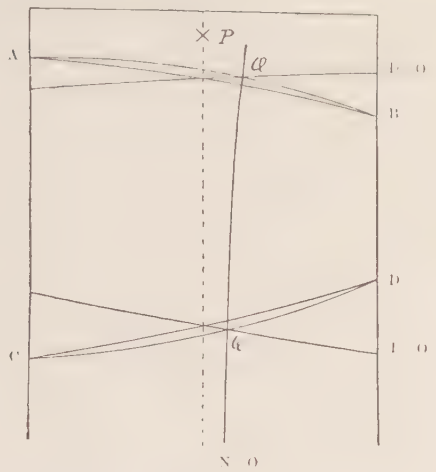

Fig. 2.

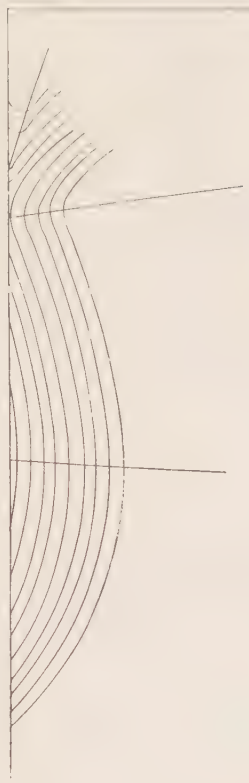

Fig. 3.

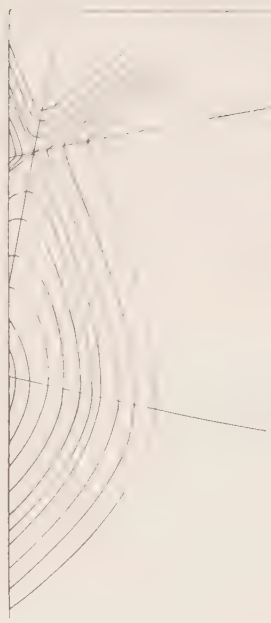

Fig. 4.

Fig. 5.

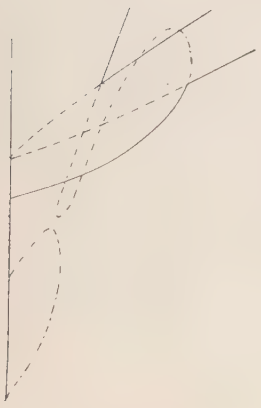

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

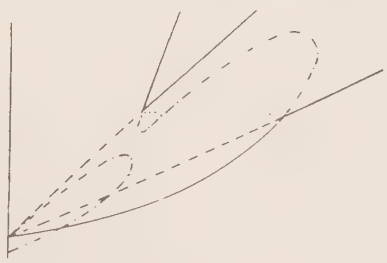

Fig. 9a.

Fig. 9b

Fig. 10.

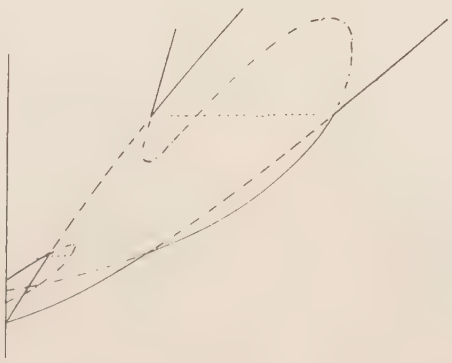

Fig. 10a.

Fig. 11

Fig. 12.

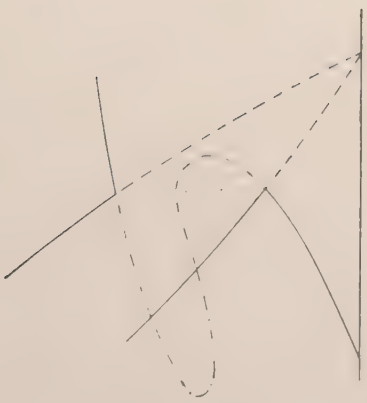

Fig. 13.

Fig. 14.

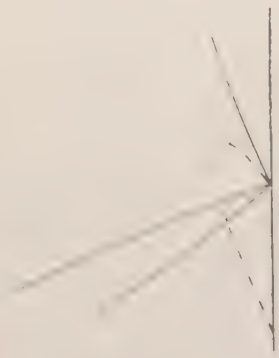

Fig. 15.

Fig. 16.

temperatures of the components given there are found in the way explained in § 5.

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atmospheric pressure according to DEWAR (Roy. Institution Weekly Evening Meetings), 25 March '04) at 0.070, and let us derive the coefficient of compressibility according to the principle of the corresponding states, e.g. from that of pentane at 20° C., then the density at 40 atms. is 0,072. If we calculate the increase of density in consequence of the solution of helium from VAN DER WAALS' equation of state for a binary mixture by putting $b_{M\mathrm{He}} = \frac{1}{2} b_{M\mathrm{H_2}}$ for this correction term, we get for the density of the liquid phase at the p and T mentioned if it contained 3 % He : 0.077.

The gas phase will have the same density at about the p and T mentioned (cf. Comm. N°. 96*a*, Nov. '06, p. 460). The theoretical density (AVOGADRO-BOYLE-GAY-LUSSAC) at $T=20°$ and $p=40$ atms. $=$ 0.0885. If we assume VAN DER WAALS' equation of state with a_x and b_x for constant x not dependent on v and T, to hold for this gas phase, it follows with the above given value of the density that $\frac{b_x}{v-b_x} - \frac{a_x}{RT}\frac{1}{v} = 0.15$.

For $a_{22} = a_{12} = 0$ with $a_{11M} = 0.00042$ (KOHNSTAMM, LANDOLT-BÖRNSTEIN-MEYERHOFFER's Physik. Chem. Tabellen), and with $v_M = 0.0021$, putting $x = 0.80$ for the gas phase, we should obtain: $b_{xM} = 0.21\ v_M = 0.00044$. We should then, if we may put $b_{12M} = \frac{1}{2}(b_{11M} + b_{22M})$, get $b_{22M} = 0.00033 = {}^3/_8\, b_{11M}$ ($b_{11M} = 0.00088$, KOHNSTAMM l. c.). If we wish to assume positive values for a_{12} and a_{22} (cf. Comm. N°. 96*a*, p. 460), we should have to put $b_{22M} > {}^3/_8\, b_{11M}$ for $T = 20°$; if we assumed that the gas phase contained 15% He we should derive from the above mentioned experiment for positive values of a_{11} and a_{12} : $b_{22M} > 0.31\, b_{11M}$.

These results harmonize very well with what may be derived about $b_{M\mathrm{He}}$ at 0° C.; the ratio of the refracting powers (RAYLEIGH) gives: $b_{22M} = 0.31\, b_{11M}$, while the ratio of the coefficients of viscosity and also that of the coefficients of the conduction of heat lead to a greater value for $b_{M\mathrm{He}}$ (about $1/2\ b_{M\mathrm{H_2}}$).

If we take $b_{22M}/b_{11M} = 1/2$, we should obtain from the above given considerations (putting $a_{12M} = \sqrt{a_{11M}\, a_{22M}}$): $a_{22M}/a_{11M} = 1/175$, so that $T_{k\mathrm{He}} =$ about 0.35°. This renders a value for the critical temperature of He $< 0.5°$ probable.

This conclusion would not hold if b_{xM} for $x = 0.8$ were considerably greater than follows from the hypothesis that b_{xM} varies linearly with x. This however is according to the experiments of KUENEN, KEESOM and BRINKMAN on mixtures of $CH_3Cl - CO_2$ and $CO_2 - O_2$, not to be expected. The experiments of VERSCHAFFELT on mixtures of $CO_2 - H_2$ would admit the possibility, but give no indication for the probability of it. [Added in the English translation].

So though probably b_{22}/b_{11} for mixtures of He and H_2 is larger, yet we shall here retain the supposition made in § 5 on b_{22}/b_{11}, with which the calculations were started, because the accurate amount is not yet known to us, and we only wish to give here an example for discussion; moreover the course of the ψ-surface will not be considerably modified by this difference in any essential respect.

TABLE I.

Barotropic plaitpoints at $M_2/M_1 = {}^1/_2$, $v_{k_2}/v_{k_1} = {}^1/_8$.

T_{k_2}/T_{k_1}	$x_{b\rho l}$	$v_{b\rho l}/v_{k_1}$	$T_{b\rho l}/T_{k_1}$	$p_{b\rho l}/p_{k_1}$
0.0002	0.6	0.3957	1.005	4.805
0.0210	0.65	0.3481	0.934	4.772
4/121	2/3	1/3	441/484	576/121
0.0604	0.7	0.3048	0.867	4.758
0.1044	0.75	0.2636	0.800	4.780
0.1472	0 8	0.2234	0.726	4.811
0.1842	0.85	0.1833	0.638	4.800
0.2106	0.9	0.1424	0.521	4.567
0.2176	0.925	0.1212	0.444	4.202
0.2190	0.94	0.1081	0.387	3.751
0.2182	0.95	0.0991	0.343	3.282
0.2148	0.965	0.0851	0.266	2.107
0.2106	0 975	0.0752	0.204	0 687
0 2040	0 985	0.0644	0.130	— 1.927
0.1996	0.99	0.0585	0.078	— 5.191
0.1960	0.995	0.0518	0.033	— 9.723
0.1956	0.9965	0.0495	0.028	—10.326
0.1964	0.9975	0.0478	0.019	—12.086
1/4	1	1/24	0	— 27

For so far as the assumed suppositions hold, the barotropic plaitpoints given in the table have only physical significance if $T_{b\rho l}$ does not become so low that solid phases make their influence felt (cf. Comm. N°. 96*b*, § 5 *b*), and if moreover the portion of the ψ-surface in the neighbourhood of the plait-point is not covered by a portion of the derived surface indicating more stable equilibria (as e. g. will be the case for negative pressures). In how far the indicated barotropic plaitpoints will belong to the gas-liquid-plait will be more fully treated in a following communication (cf. footnote 2, p. 660).

In the first place it follows from table I that with the assumed

ratios of the molecular weights and of the critical volumes, barotropic plaitpoints prove only possible (quite apart from the question whether they are physically realisable, and whether they belong to the gas-liquid plait) for $T_{k_2}/T_{k_1} < \frac{1}{4}$.

The barotropic plaitpoint for the ratio $T_{k_2}/T_{k_1} = 0.0002$ is a plaitpoint for a mixture, one component of which is a gas almost without cohesion (Comm. No. 96*b* § 1). A further consideration of it would lead us again to the region of the longitudinal plait.

The conditions relating to barotropic plaitpoints for x_{bpl} near 1 furnish a contribution to the knowledge of VAN DER WAALS' ψ-surface for binary mixtures with a small proportion of one of the components [1]). We find for T_{k_2}/T_{k_1} near $^1/_4$, putting $x_{bpl} = 1 - \xi$:

$$u = -\xi^{-2/3}\left\{1 - \frac{1}{2}\xi^{2/3} - \frac{1}{3}\xi \ldots\right\}, \mu = -\frac{9}{7}\left\{1 - \frac{4}{9}\xi^{1/3} + \frac{20}{9}\xi^{2/3} - \frac{29}{9}\xi \ldots\right\}, T_{k_2}/T_{k_1} = \frac{1}{4}\left\{1 - \frac{7}{2}\xi^{1/3} + \frac{315}{16}\xi^{2/3} - \frac{735}{16}\xi \ldots\right\}.$$

It is seen from the series of the ratios T_{k_2}/T_{k_1} in table I, that in this a maximum and a minimum occur, respectively for about $T_{k_2}/T_{k_1} = 0.219$ and 0.196. From the formulae derived for x_{bpl} near 1, a minimum and a maximum for μ is found, and hence for T_{k_2}/T_{k_1}, respectively at $x_{bpl} = 0.9968$ and 0.969. That the latter is in reality found at $x_{bpl} = 0.94$ is due to following terms in the development.

For $T_{k_2}/T_{k_1} < 0.196$ or $0.219 < T_{k_2}/T_{k_1} < 0.25$ one barotropic plaitpoint is found, for $0.196 < T_{k_2}/T_{k_1} < 0.219$ three. In connection with Comm. No. 96 *b* § 2 (Dec. '06 p. 502, cf. also this Comm. § 1, Dec. '06, p. 508) it follows also from this that for the mixtures considered here at lower temperature the longitudinal plait makes its influence felt.

The experiment described in Comm. N°. 96*a* proved that for mixtures of He and H_2 at $-253°$, i.e. about $T = 0.65\ T_{kH_2}$, a barotropic tangent chord is found on the ψ-surface. If at that temperature only *one* barotropic tangent chord occurs, this will point to this (Comm. N°. 96*b* p. 504) that for the mixtures of these substances $T_{bpls} > 0.65\ T_{kH_2}$, and therefore according to this table $T_{kHe} < 0.18\ T_{kH_2}$, while the found considerable difference in concentration between the gas and the liquid phase (see Footnote 3,

[1]) Cf. Comm. N°. 75 (Dec. '01), N°. 79 (April '02), N°. 81 (Oct. '02), Suppl. N°. 6 (May, June '03).

p. 660) indicates, that T_{bpls} would have to lie still pretty much higher, and therefore T_{kHe} pretty much lower (probably $<$ about 4°) [1]. Of this result we availed ourselves in the treatment of the estimation of the critical temperature of He in Comm. N°. 96*b*.

(To be continued).

Physics. — "*Contributions to the knowledge of the ψ-surface of* VAN DER WAALS. XIV. *Graphical deduction of the results of* KUENEN'S *experiments on mixtures of ethane and nitrous oxide.*" Supplement 14 to the Communications from the Physical Laboratory of Leiden. By Prof. H. KAMERLINGH ONNES and Miss T. C. JOLLES.

(Communicated in the meeting of Januari 26, 1907).

§ 1. *Introduction.* In what follows we have endeavoured to derive quantitatively by first approximation the behaviour of the mixtures of N_2O and C_2H_6 (mixtures of the II type [2]), which has become known through KUENEN'S experiments [3]), by the aid of VAN DER WAALS' free-energy surface. The ψ-surfaces construed for this purpose (see plate I) are the counterparts of those construed in Comm. N°. 59 (These Proc. Sept. 1900) and Comm. N°. 64 [4]) for the derivation of the results of KUENEN'S and HARTMAN'S experiments on mixtures of CO_2 and CH_3Cl (mixtures of the I type). In the graphical treatment [5]) of our problem we have chiefly followed the method given in Comm. N°. 59, where the critical temperature and pressure of some mixtures were borrowed from KUENEN'S determinations, and then the results of another group of experiments — those referring to the conditions of coexistence of two phases at a certain temperature — were deduced by the aid of VAN DER WAALS' theory.

KUENEN'S results for N_2O and C_2H_6 are principally laid down in

[1]) If b_{22}/b_{11} is taken larger than $1/8$ (Cf. Footnote 3 p. 660) this supposition too makes the upmost limit for T_{kHe} on the said supposition smaller. This is seen when we compare with table I that we obtain $T_{bpl}/T_{k_1} = 0.679$ for $b_{22}/b_{11} = 1/4$ with $T_{k_2}/T_{k_1} = 0.15$.

[2]) HARTMAN, Leiden Comm. Suppl. no. 3, p. 11.

[3]) KUENEN, Leiden Comm. no. 16, Phil. Mag. 40, p. 173, 1895, cf. also KAMERLINGH ONNES and ZAKRZEWSKI, Leiden Comm. Suppl. no. 8. (These Proc. Sept. 1904). It is remarkable that the possibility of this case was foreseen by VAN DER WAALS, Contin. II, p. 49 [added in the English translation].

[4]) Arch. Néerl. Serie II, Tome V, p. 636.

[5]) Only graphical solutions for definite cases are here possible. (Cf. Suppl. 8, These Proc. Sept. 1904. § 1).

four figures [1]); one of them gives the critical quantities from which we shall start in our deduction, and the border curves for mixtures of different concentration; the three others, which represent the xv-projection of the connode with the connodal or tangent chords at the temperatures 20° C, 25° C, 26° C, show the contraction of the transverse plait with rise of temperature, and finally its splitting up into two plaits.

We have thought that we could obtain a better comparison of observation and calculation, when representing the observations by the xv-figures for 5° C., 20° C. and 26° C., and the pT-figure, instead of by the xv-figures at the before mentioned temperatures and the pT-figure.

§ 2. *Basis of the calculation. Law of the corresponding states and reduced equation of state.* We start (cf. Suppl. N°. 8, These Proc. Sept. 1904 § 1) from the supposition that the law of the corresponding states — at least within the region of the observations — holds as well for C_2H_6 and N_2O as for their mixtures. As reduced equation of state we chose equation V. s. 1 of Comm. N°. 74[2]) p. 12 For a region of reduced temperature and pressure which incloses the region which corresponds to that of the observations under investigation, this equation is as closely as possible adjusted to CO_2, which in thermical properties has much in common with N_2O, and there is no reason to suppose that this will not be the case with C_2H_6.

In the application we are, however, confronted by this difficulty, that V. s. 1 deviates most strongly from the observations on CO_2 exactly in the neighbourhood of the critical state. (Cf. Comm. N°. 74 and later KEESOM, Comm. N°. 88). If from V. s. 1 [3]) the point is derived, for which

$$\frac{\partial p}{\partial v} = 0 \text{ and } \frac{\partial^2 p}{\partial v^2} = 0 ,$$

we find $t = 1.010595$, $\lambda v = 1.0407.10^{-3}$, $p = 1{,}06566$. KEESOM's observations, Comm. N°. 88, give for the critical volume, when it is sought by the application of the law of the rectilinear diameter, for CO_2

$$v_k = 0.00418 \text{ and for } \lambda = \frac{p_k v_k}{T_k} = 1.0027.10^{-3}. \quad . \quad . \quad (1)$$

---

1) Where it was necessary, KUENEN's figures have been rectified in accordance with the results of observation given by him.

2) Arch. Néerl. Vol. Jubil. Bosscha. Serie II, tome 6, 1901.

3) In the calculations T is put 273°,04 for the freezing point of water, because V. s. 1 was calculated with this value.

We find then:

$$t_k = 1.010595 \text{ instead of } t_k = 1$$
$$v_k = 1.0379 \quad ,, \quad ,, \quad v_k = 1$$
$$p_k = 1.06566 \quad ,, \quad ,, \quad p_k = 1.$$

The isotherms from which V. s. 1 has been derived by the computation of the virial coefficients $\mathfrak{B}$, $\mathfrak{C}$ etc. (See comm. N°. 71, These Proc. June 1901), indicate therefore, by means of interpolation according to this mode of calculation, a critical state, which, drawn in the pv-diagram, has shifted with respect to that which was found by immediate observation; the critical temperature according to V. s. 1 is namely $t_k T_k$ when T_k is the observed critical temperature.

So are also the values found for $p_{max.}$, v_{liq} and $v_{vap.}$ at t by the application of MAXWELL's criterion, different from those which we should find when dividing $p_{max.}$ by p_k, $v_{liq.}$ and $v_{vap.}$ by v_k. The deviations are of the same order as the deviations of the substances inter se, when they are compared by the law of the corresponding states. At $t = 0{,}9$ they are about zero, but they increase as we approach the critical state, so that the deviations agree with a gradual transformation of the net of isotherms. The following table gives a survey of the deviations in the corresponding values.

Column A refers to V.s. 1 and implicitly to p_k, T_k of CO_2
,, B ,, ,, the observations ,, CO_2
,, C ,, ,, ,, ,, ,, N_2O.

A		B		C	
t	p	t	p	t	p
1.0106	1.066				
		1.	1.	1.	1.
0.975	0.826	0.975	0.845	0.975	0.854
0.950	0.695	0.950	0.709	0.950	0.720
		0.925	0.589	0.925	0.599
0.900	0.490	0.900	0.494	0.900	0.486

In the neighbourhood of the critical temperature the phenomena are governed by the difference of the temperature of observation and the critical temperature, $T - T_k$; for this reason we have chosen for the detailed model of 26° such a temperature T' for the com-

parison of the observations at that temperature T with the result of computation that

$$T_k - T = t_k T_k - T'.$$

At the general survey for 26° we have applied to $t = \frac{T}{T_k}$ a correction $= \Delta t$, so that $\Delta t = 0.0106\,\theta$, when $\theta = 10(t - 0{,}9)$ for $0 < \theta < 1$, whereas $\Delta t = 0$ for all other values of θ. The correction Δt to t was accompanied by a correction Δv to v and Δp to p, so that $\Delta p = 0\,0657\,\theta$ and $\Delta v = 0.0379\,\theta$, which together represent a regular increase of the corrections from $t = 0{,}9$ to the critical state. For the detailed model of the ψ-surface for 26°, on which only the part from $x = 0{,}35$ to $x = 0{,}65$ was represented, we used everywhere the same correction viz. $\Delta t = 0.0106$, $\Delta p = 0{,}0657$, $\Delta v = 0{,}0379$.

§ 3. *Critical quantities for the mixtures.* KUENEN has determined the plaitpoints $T_{pl.x}, p_{plx}, v_{pl.x}$, for some mixtures with the molecular concentration x. T_{rx}, p_{rx}, v_{rx}, the critical points of contact, and T_{kx}, p_{kx}, v_{kx} the critical states of the mixtures taken as homogeneous differ so little [1]) from these values, that this difference may be disregarded for our purpose, and so they are also known for the mixtures investigated by KUENEN.

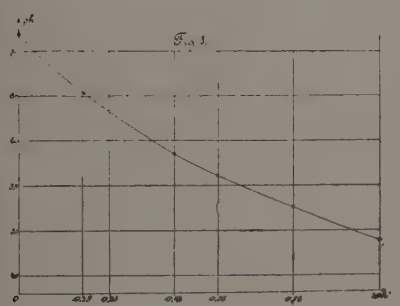

Fig. 1.

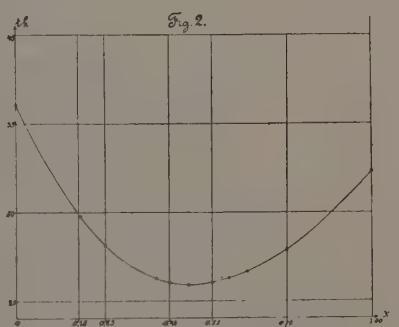

Fig. 2.

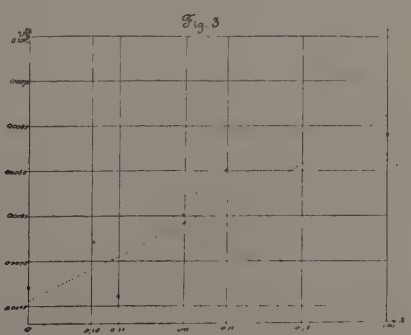

Fig. 3

[1]) This has been fully treated by VAN DER WAALS, Cont. II, § 11.

The critical quantities for the other mixtures were found by graphical interpolation. Fig. 1 gives p_{kx}, fig. 2 T_{kx} as function of x; in fig. 3 v_{kx} has been calculated from p_{kx} and T_{kx}, by the aid of λ (see formula (1)); the v_{kx} observed by KUENEN have been indicated there.

By carrying out the construction for the connode by the aid of the p, $\frac{\partial\psi}{\partial x}$ and $\psi - x\frac{\partial\psi}{\partial x} - v\frac{\partial\psi}{\partial v}$ curves (see Comm. N°. 59a[1])), which the models for those different temperatures yield, we may derive $v_{kx} - v_{pl.x}$, $p_{kx} - p_{pl.x}$ in first approximation (see Comm. N°. 59a). Applying these corrections we should then have to repeat the calculation from the beginning, to obtain more accurate values for v_{kx}, p_{kx}. We have confined ourselves to a first approximation in all our constructions, as also a further correction of the equation of state V.s. 1., which can cancel the deviations mentioned in § 2, has not been applied and we were the more justified in this, as these latter deviations are larger than those we have now in view.

§ 4. *Construction of the ψ-surfaces.*

From the equation of state V. s. 1 we find immediately the reduced $\psi_x T$ curves, from which are then deduced the ordinary ψ-curves according to Suppl. N°. 8, § 4; or the ordinary virial coefficients, whic hare then used for the calculation of ψ according to Comm. N°. 59.

For the construction (cf. Comm. 59) use was made of:

at 5° $\quad \psi'_5 = \psi + 0{,}10\,x + 25\,v$

„ 20° $\quad \psi'_{20} = \psi + 0{,}10\,x + 36{,}5\,v$

„ 26° $\quad \psi'_{26} = \psi + 0{,}24\,x + 57{,}3\,v,$

while a suitable constant was subtracted from every ψ. Here v is expressed in the theoretical normal volume, just as in the diagrams. From the $\psi_x T$ curves (cf. fig. 1, pl. II) the $\psi_v T$ curves (see fig. 2, pl. II) and the p_T curves were graphically derived. The models for ψ were construed on a scale 5 times larger than the diagrams on pl. II, pl. III and pl. IV.

§ 5. *Determination of the coexisting phases.*

Applied was both the construction by rolling a glass plate on the

[1]) In giving the figure 3 in Comm. N°. 59a for this construction it was stated that this figure was very imperfect. It appears now that the loop ought to contain two cusps. We found out the error by the aid of the general properties of the substitution-curves treated by VAN DER WAALS (Comp. Proceedings of this meeting). This error shows the more how necessary it is that graphical solutions are controlled by such general properties as VAN DER WAALS is now publishing. [Added in the English translation].

model, which yields the connode and the tangent chords, and the simplified construction in the plane given in Suppl. N°. 8, § 7, to which a small correction was applied. After viz., a provisional connode, that of the mixtures taken as homogeneous, has been found by tracing curves of double contact to the ψ_{xT}-curves, and by determining conjugate points b on the gas branch at some points a on the liquid branch of that connode, so that every time $\frac{\partial \psi}{\partial x}$ is the same for the two conjugate points, the lines which join every two of these points a and b, are produced outside the provisional connode, till they cut the isobars which pass through a, in points c, which together represent the required gasbranch of the connode; c and a are then considered as conjugate points. In the ψ-surface at 5° C. the two constructions yielded fairly well corresponding results, both with regard to the chords and to the connode itself, as appears from pl. II fig. 4, where — — — — denotes the connode and the connodal tangent-chords found by rolling a glass-plate on the model, —.—.—.— those found by means of the just mentioned construction. That the simplified construction, which was more particularly plotted for equilibria far below the critical temperature (see Suppl. N°. 8, § 7) still leads to our end, is probably due to the fact, that we have here to deal with a mixture of the II type.

With the ψ-surface for 20° the slight depth of the plait rendered it necessary, to considerably diminish the longitudinal scale for the v-coordinate of the model. This compression (cf. pl. I, fig. 2) rendered the plait sufficiently clear to determine the connode and the place of the connodal tangent chords by rolling a glass plate. By means of the simplified construction the connode was still to be obtained, but the determination of the tangent-chords became uncertain.

With the ψ-surface of 26° the depth of the plait (here split into two) becomes so exceedingly slight, that it does not appear but with a computation with 7 decimals, and even then it manifests itself almost quite in the two last decimals. Hence it is not possible to model a ψ'-surface (we mean a surface derived from the ψ-surface, on which the coexisting phases are still to be found by rolling a plane), on which this plait is visible, nor is it of any avail to confine ourselves to a small part of the surface, because the curvature of the ψ_{vT}-curves is very strong exactly there where something important might be shown. The determination of the connode and the connodal tangent chords by construction according to § 8 of Comm. N°. 59a, which can always be carried out provided enough decimals are worked with, remained still uncertain up to 7 decimals, so that we have

not pursued it any further. Thus the represented part of the ψ-surface for 26° from $x=0.35$ to $x=0,65$ and from $v=0.0038$ to $v=0.0070$, has been given by us chiefly to demonstrate how exceedingly small the influences must be on which a plait depends, and how much care is required to determine a plait experimentally which is not at all to be seen on the surface. The curves drawn on the surface, which relate to the plait, were found by indirect ways, partly by construction, partly by calculation. To facilitate a comparison of the models inter se the region of x and v, on which the model for 20° and that for 26° extends, has been indicated on the model for 5°, on the model for 20° that for 26°.

§ 6. *Further remarks on the different models and drawings obtained by construction.*

a. The ψ'-surface for 5°. The model, pl. I, fig. 1, and the drawings pl. II, figs. 1, 2 and 3 show curves of equal concentration, ψ'_{xT}, equal volume and equal pressure, the connode and the connodal tangent chords. As $-\frac{\partial\psi'}{\partial v}=p-25$, some pressures are represented by negative slopes on the stable part of the ψ'-surface, in consequence of which the character of this ψ'-surface does not in this respect immediately express that of the ψ-surface, where all the slopes are positive. A connodal tangent-chord, near the concentration with maximum pressure, almost touches the ψ_x-line. With the concentration of maximum pressure this would be just the case. Just as the connodal tangent chords the isobars are traced in the projection on the $x\,v$-plane (Pl. II, fig. 3) in full lines, the connode is denoted by —.—.—.

For the isobars [1]) we may note several peculiarities, to which VAN DER WAALS has drawn attention in his theory of ternary systems [2]). The isobar which touches the connode on the liquid and vapour side, belongs to the pressure $p=36,6$, which is found for the mixture which when behaving as a simple substance should have a maximum coexistence pressure. The pressure curve π determines the transition between the continuous isobars (taking the region outside the drawing into consideration) and those split up into two branches. The parts of the continuous isobars which point to P, have each a point of inflection on either side of the top. The shape of the curves $\frac{\partial^2\psi}{\partial v\partial x}=0$ and $\frac{\partial^2\psi}{\partial v^2}=0$

[1]) Cf. the sketch by HARTMAN, Leiden Comm., Suppl n°. 3, pl. II, fig. 5.

[2]) These Proc. March 1902, p. 540.

is as has been indicated by VAN DER WAALS [1]). The points of intersection of these two curves are the centre Q of the isobars and the double point of the pressure curve π, P.

b. The ψ'-surface for 20°. Fig. 1, pl. III denotes the ψ_{xT}-curves and the connode. Fig 2, pl. III the ψ_{vT}-curves and the connode. Fig. 3 gives the projection on the xv-plane of the connode, of the tangent chords and of some isobars. The connode is denoted by —.—.—. Pl. I fig. 2 gives a representation of the model.

c. The ψ'-surface for 26°. Fig. 1 pl. IV gives the ψ_{xT}-curves, fig. 2 pl. IV gives the critical states, K_1 and K_2 the isobars and the connodes for the mixtures which are taken as homogeneous, and whose gas branch as well as whose liquid branch is almost a straight line. Though in the calculations (see § 2) the plaitpoint x_{Tp} and the critical point of the homogeneous mixture x_{Tk}, have been considered as coinciding, a distance has now been given between these points which has been fixed by estimation [2]). The dotted parabola has been taken from VERSCHAFFELT's calculation, Suppl. N°. 7, p. 7, though properly speaking it holds only for the case that the maximum pressure falls in P_1 or P_2; the produced connode denotes the probable course of this part by approximation. Pl. I, fig. 3 gives a representation of the model. All this refers to a small region of x and v; fig. 3 pl. IV, however, indicates by —.—. —.—. the connode according to the construction for the mixtures taken as homogeneous all over the width of the ψ'-surface. The square drawn denotes the extension of the just treated part of the ψ'-surface.

d. The contraction and the subsequent splitting up of the plait appears from fig. 4 Pl. III, where the xv-projections of the connode and some connodal tangent chords of the three models have been drawn on the same scale after the xv-figures for 5°, 20° and 26° mentioned under *a b c*.

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[1]) Prof. VAN DER WAALS was so kind as to draw our attention to a property which might also have been represented in the figure, when also the curve for $\frac{\partial^3 \psi}{\partial v^2 \partial x} = 0$ had been drawn, viz. that the minimum volume in the vapour branch, and the maximum volume in the liquid branch lie on the curve $\frac{\partial^3 \psi}{\partial v^2 \partial x} = 0$ which has a course similar to that of the curve $\frac{\partial^2 \psi}{\partial v \partial x} = 0$, more particularly it has the same asymptotes, and it deviates from it only in this, that with greater density the curve passes over larger volumes.

[2]) Here the representation of the plait must come into conflict with the theory or with the simplification introduced at the basis of the calculation. With a view to the illustration of the theory by figures the latter has been chosen.

§ 7 *Comparison of the construction with the observation.* On the whole this is very satisfactory, taking the degree of approximation into consideration.

a. In pl. II fig. 4 the diagram for the plait at 5° indicating KUENEN's observations, has been drawn in full lines. The figure contains at the same time that obtained by construction. The single observations have been denoted by ⊡ (see § 6*a*). Besides the construction with the model indicated by — — — — and by ⊽, also the simplified constructions in the plane indicated by —.—.— and by ⊙, the outermost of which refers to the less simplified construction, represent the character and also the numerical values satisfactorily.

b. In pl. III, fig. 3 the figure representing KUENEN's observations for the plait of 20°, has been indicated by — — — —. The figure contains at the same time the —.—.—., obtained by construction on the model (see § 6*b*). The correspondence at $x = 0.3$ is the worst, which is no doubt in connection with this, that here we have already got very near the critical temperature, and that strictly speaking, different values should be assigned to T' (see § 2) for all x, and corresponding $\Delta\mathfrak{v}$ and $\Delta\mathfrak{p}$ should have been taken into consideration.

c. In pl. IV fig. 3 the figure representing KUENEN's observations, have been indicated by full lines; the figure contains also the figure derived in § 6*c* denoted by —.—.— curves.

d. Plate IV fig. 4 and 5 may serve for a comparison of KUENEN's pT-figure (fig. 4) with that derived by construction (fig. 5). In accordance with the remark on T' in § 2, we have proceeded for 26° as follows:

For 5° and 20° the values of p and T have simply been taken from the construction with the model, mentioned under *a* and *b*. Then we marked *α*) the p's and T's, obtained by multiplying KUENEN's p_k and T_k by $\mathfrak{p}_k$ and t_k (see § 2); *β*) for the different values of x the values of T' and of θ for the temperature of 26° have been calculated, and then Δt and $\Delta\mathfrak{p}$ determined by the aid of this θ according to § 2; the values of p and T corrected in this way have been denoted by + + + and joined by —.—. ..— curves with the points mentioned under *α*). The full and the dotted curves give the corrected values. Between the parts where we started from the critical temperature, and the pT-lines derived fromthe models of 5° and 20° a space has been left open.

H. KAMERLINGH ONNES and Miss T. C. JOLLES. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XIV. Graphical deduction of the results of KUENEN'S experiments on mixtures of ethane and nitrous oxide.

Plate I.

Fig. 1.

Fig. 2.

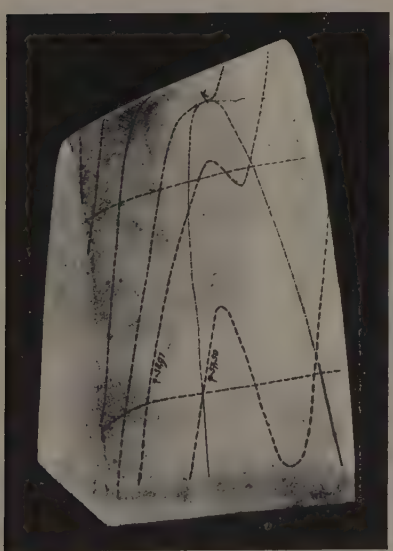

Fig. 3.

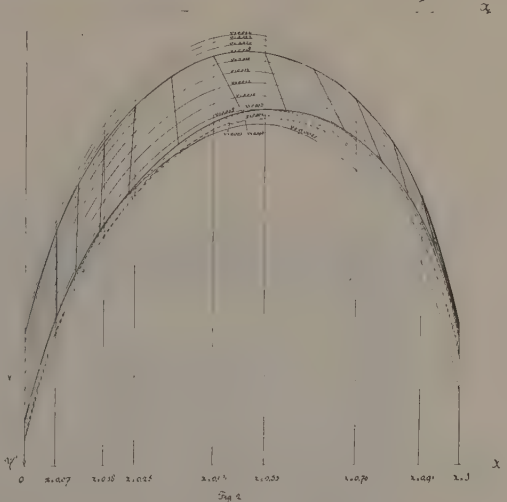

Fig 2

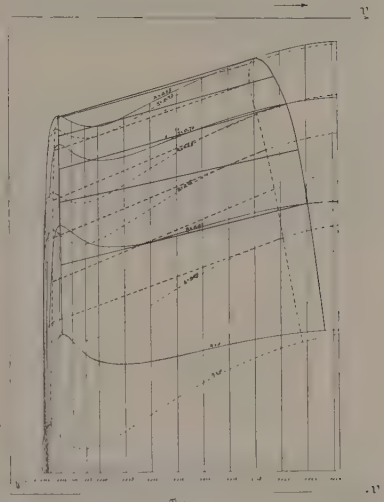

Fig 1

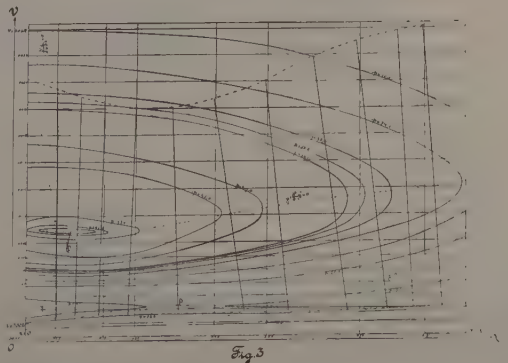

Fig. 3

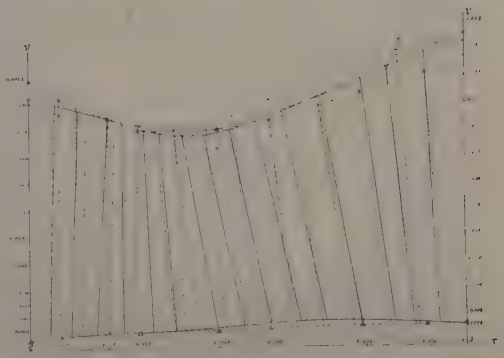

Fig. 4.

H. KAMERLINGH ONNES and Miss T. C. JOLLES. Contributions to the knowledge of the ψ-surface of VAN DER WAALS. XIV. Graphical deduction of the results of KUENEN's experiments on mixtures of ethane and nitrous oxide.

Plate III.

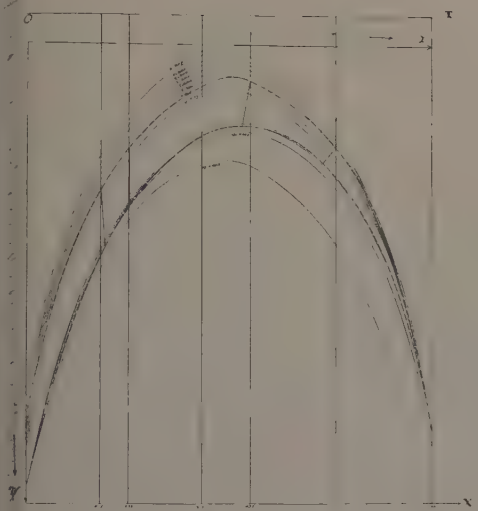

Fig 2.

Fig. 1.

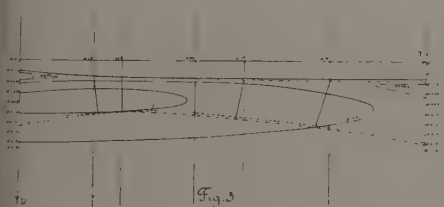

Fig. 3

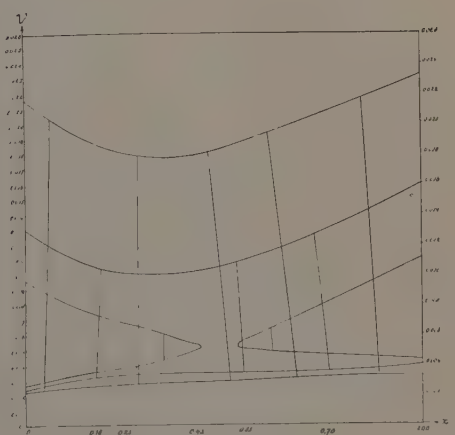

Fig. 4.

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Plate IV.

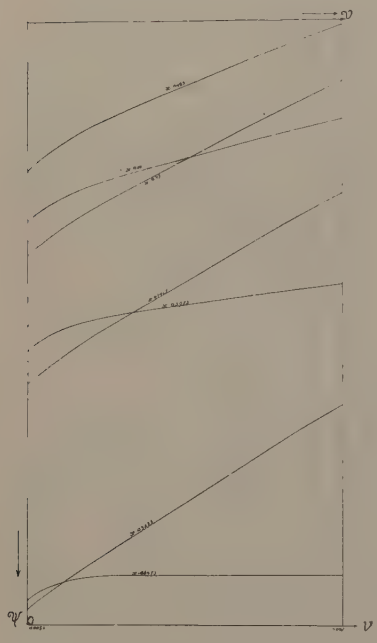

Fig. 1.

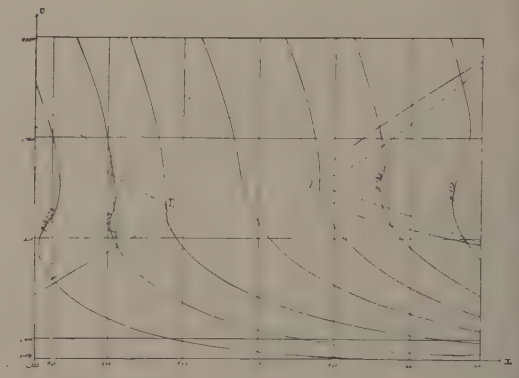

Fig. 2.

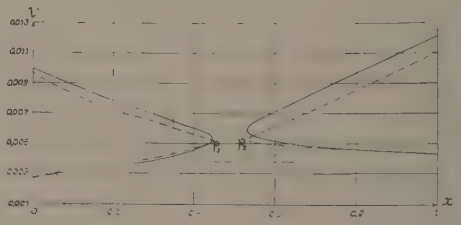

Fig. 3.

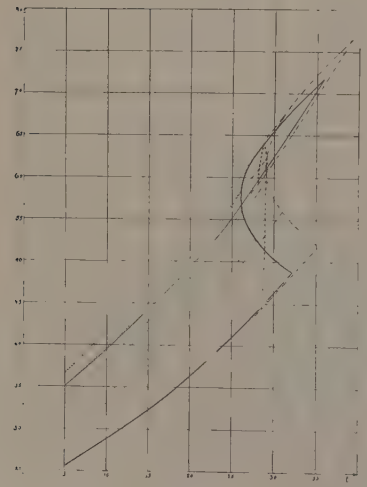

Fig. 5.

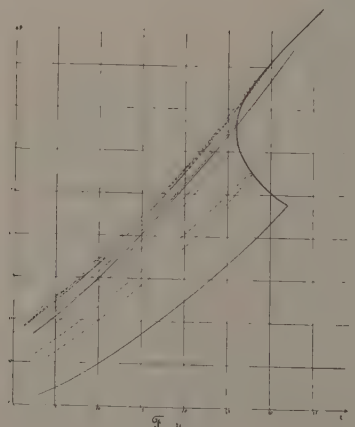

Fig. 4.

Pathology. — "*On the Origin of Pulmonary Anthracosis.*" By P. NIEUWENHUIJSE. (From the Pathological Institute in Utrecht). (Communicated by Prof. C. H. H. SPRONCK.)

(Communicated in the meeting of January 26, 1907).

As is known, von BEHRING and CALMETTE oppose the doctrine according to which the pulmonary tuberculosis among mankind proceeds in most cases from inhalation or aspiration of tuberclebacilli. They presume the tractus intestinalis to be the porte d'entrée of the virus.

In connection with this new hypothesis VANSTEENBERGHE and GRISEZ [1]) have made some experiments at the end of 1905 in CALMETTE's laboratory about the origin of lung-anthracosis.

They mixed the food of full-grown cavies with soot, Indian ink or carmine and made the animals eat a large quantity of this. After 24 hours already they found resp. black and red spots in the lungs especially in the upperlobes and along the edge of the underlobes.

VANSTEENBERGHE and GRISEZ concluded from these results that the fine parts, taken up in the intestines, pass through the mesenteric glands and thoracic duct and after having reached the blood in this way, they are caught by the lungs.

According to their conclusion the carbon particles suspended in the atmosphere would not be inhaled, but swallowed, thus reaching the lungs via the intestines. The theory of the intestinal origin of the pulmonary anthracosis was propounded half a century ago by VILLARET [2]); it had however met with little success, and after the careful researches made by ARNOLD [3]) on the inhalation of fine particles it was totally forgotten.

Whereas VANSTEENBERGHE and GRISEZ tried to defend the theory of VILLARET, after having made new experiments and no less a person than VON BEHRING doubted the exactness of the generally assumed opinion, no one will be surprised that criticism soon followed.

Whilst I was working in the laboratory of Prof. SPRONCK, to whom I offer my thanks for his continual interest in this research, repeating the experiments of VANSTEENBERGHE and GRISEZ, several treatises appeared on this subject. First of all ASCHOFF [4]) advanced

[1]) Annales de l'Institut Pasteur, 1905, p. 787.

[2]) VILLARET: Cas rare d'anthracosis, Paris, 1862, ref. in Schmidt's med. Jahrb. 1862, Bd. 116.

[3]) ARNOLD: Untersuchungen ueber Staubinhalation und Staubmetastase, Leipzig, 1885

[4]) Sitzungsber. der Gesellschaft zur Bef. der Ges. Naturwissenschaft, Marburg, 13 Juni, 1906.

the opinion that there must have been technical mistakes in the experiments of VANSTEENBERGHE and GRISEZ; some time afterwards he was enabled to convince himself of the incorrectness of their opinion by his own experiments [1]).

MIRONESCO [2]) after bringing fine particles into the stomach of rabbits, was not able to recover them in the lungs.

In August 1906 VANSTEENBERGHE and SONNEVILLE [3]) described a new series of experiments which confirmed the results of VANSTEENBERGHE and GRISEZ.

Fine particles which were brought into the mouth with a catheter were already to be recognised in the lungs after a lapse of 5 or 6 hours.

Soon afterwards the opinion of VANSTEENBERGHE and GRISEZ was opposed by two authors: SCHULZE [4]) in a temporary publication concluded that the pulmonary anthracosis could not proceed from the resorbing of fine particles from the intestines and Prof. SPRONCK communicated shortly afterwards at the 5th International Conference on Tuberculosis the results of some of the following experiments, which were adverse to the results, gained by VANSTEENBERGHE and GRISEZ.

In a more extensive treatise SCHULZE [5]) demonstrated further how substances are lightly aspirated into the lungs either by administering them with the catheter or by ordinary eating. A rabbit however, had received within two months the total quantity of 200 grams of vermillion through a gastrotomy, yet no trace of vermillion was to be found in the lungs.

On the other hand some investigators took the part of VANSTEENBERGHE and GRISEZ: PETIT [6]) brought carbon particles into the stomach of six children who were in an advanced state of tuberculosis or athrepsy and after a post-mortem examination he found pigment in the lungs in three of them and HERMANN [7]), on the authority of experiments, esteemed an intestinal origin of the lung-anthracosis possible, but compared with the inhalation-anthracosis of very inferior significance.

Afterwards the results of VANSTEENBERGHE and GRISEZ were empha-

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[1]) BRAUER's Beiträge zur Klinik der Tuberculose, 1906, Bd VI, Heft 2.
[2]) Compt. rend. de la Soc. de Biol. 1906, T. 61, N°. 27.
[3]) Presse médicale, 11 Août 1906.
[4]) Münchener Med. Wochenschr. 1906, N° 35.
[5]) Zeitschrift für Tuberculose, October 1906.
[6]) Presse médicale, 13 Octobre 1906.
[7]) Bulletin de l'Académie royale de médecine de Belgique, Séance du 27 Octobre 1906. La Semaine médicale, 1906, N° 44.

tically contradicted from various sides. (COHN[1]), REMLINGER[2]), BASSET[3]), KÜSS et LOBSTEIN[4]), BEITZKE[5])).

Some of the above mentioned considered the normal anthracosis in test-animals as a source of mistakes, which VANSTEENBERGHE and GRISEZ had not taken into account whereas others described the aspiration also as a source, which might give rise to wrong conclusions.

Meanwhile VANSTEENBERGHE and GRISEZ, supported by CALMETTE[6]) maintained their opinion. They explain the negative results of their opponents in the following manner: some allowed too much time to pass between the introducing of carbon particles into the stomach and the killing of the test-animals, because after 48 hours the pigment would have almost completely disappeared from the lungs; others used rabbits or too young cavies as test-animals, in which the fine particles are almost wholly retained by the mesenteric glands.

With a view to this last remark I wish to publish the following experiments, because I have taken into account the age of test-animals as well as the time which passed between the introduction of the fine particles and the killing of the animals.

To me it also appeared that the physiological anthracosis is a factor which must be considered, for among all my test-animals, cavies as well as rabbits, black pigment was found in the lungs.

Among some animals this spontaneous anthracosis was rather decided, with others very minute. As a rule there was much less pigment in the lungs of my rabbits than in those of the cavies.

The physiological anthracosis impedes as a matter of course the experimenting with black substances. Besides carmine, vermillion and ultramarine, I have also used Indian ink and soot, because after microscopic investigation it appeared that the first mentioned matter, even after being intensively rubbed in a mortar, was not as fine as the particles of carbon of the last mentioned.

In order to control the experiments of VANSTEENBERGHE and GRISEZ

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1) Berliner Klin. Wochenschr. 1906, N° 44 und 45.
2) La Semaine médicale, 1906, N° 45.
3) La Semaine médicale, 1906, N° 47.
4) Bulletin médical du 21 Novembre 1906.
La Semaine médicale, 1906, N° 48.
5) Virchow's Archiv, Bd. 187, Heft 1.
6) Compt. rend. des séances de l'Académie de Sciences, T. 143. p. 866.
Compt. rend. de la Soc. de Biol. T. 61, p. 548.
La Semaine médicale, 1906, N°. 50.

the test-animals were killed already 5—48 hours after administering the forementioned substances.

Some cavies (experiment n°. 1—5) had eaten bread, mixed with soot, Indian ink or carmine. After the dissection of the animals, the lungs showed only the ordinary physiological anthracosis, but carmine was to be seen neither in the lungs nor in the bronchial glands.

One of these animals (experiment n°. 4) had evidently aspirated soot, for in many bronchi and corresponding alveolars, foodparticles and soot were distinctly seen in large quantities.

Also after introducing various matters with the catheter into the stomach of rabbits (experiment n°. 6—10), aspiration was observed once (experiment n°. 10), whereas among other animals only the normal pigmentation was present.

In order to prevent aspiration with certainty, tracheotomy was performed with three rabbits and after that a suspension of carmine was brought into the stomach with the catheter (experiment n°. 11—13); for the same purpose among some cavies I injected coloured particles into the distal part of the oesophagus which was cut through and then bound up (experiment n°. 14—18). After dissecting no traces of coloured particles were to be found neither in the lungs nor in the bronchial glands.

Further with different cavies the fine particles were directly brought into the intestines after laparotomy (experiment n°. 19—35). Neither was then any of the coloured matter to be found in the lung-tissue nor in the bronchial glands, whereas everywhere else nothing was to be seen except normal anthracosis in varying intensity.

Among some experiments I noticed that coloured particles which were injected directly into the intestines, were later on to be found also in the stomach, in the oesophagus and in the pharynx, sometimes in large quantities (experiment n°. 21, 22, 29 and 30). In the phlegm of the trachea the coloured particles could be distinctly seen sometimes with the use of the microscope (experiment n°. 21 and 29), whilst once (experiment n°. 29) the easily recognisable ultramarin-grains were to be seen even in the phlegm of the chief bronchi. It is quite probable that the animals in agony had aspirated these substances from the pharynx, for, according to NENNIGER [1]) e. g. bacteria too are often aspirated from the pharynx in agony.

The question is now, how came the matter from the pharynx into the intestines. Was it by a motion of the fine particles in a

[1]) Zeitschr. f. Hygiene u. Infectionskrankheiten, Bd. 38.

proximal direction, as e. g. GRÜTZNER[1]) describes this for fine particles in the intestines and as KAST[2]) has also shown for the oesophagus, or, had the animals eaten their own faeces?[3])

In order to solve this question, four cavies were carefully wrapped in a bandage, after ultramarine had been brought into the intestines so that eating the faeces was quite impossible (experiment n°. 32—35). It now appeared that the ultramarine had come some way proximal from the place of injection, but in the oesophagus, in the pharynx and in the chief bronchi no ultramarine was discernible.

From this I suppose that the ultramarine had simply come into the pharynx owing to the eating of faeces and not through a proximal motion of the fine particles[4]).

From my experiments I conclude that the pulmonary anthracosis does not originate through taking up fine particles from the intestines. It may be acceptable à priori, that fine particles *can* be taken up in the intestinal mucous membrane and *can* get into the lungs along ductus thoracicus and right heart, but this phenomenon is with regard to the pulmonary anthracosis of not so much importance, as VANSTEENBERGHE and GRISEZ have supposed. Evidently these investigators have given sufficient attention neither to the physiological anthracosis of the test-animals, nor to the aspiration of the coloured particles which cannot be quite prevented, not even, as is mentioned above, by direct injecting the matters into the intestines.

If the physiological anthracosis originated by taking up carbon particles from the intestines, not only the mesenterial glands but also the marrow and the milt had to contain much carbon pigment, because firstly it cannot be understood how carbon parts should pass the mesenterial glands without leaving distinct traces of their passing behind them and on the other hand there is no possible reason why the carbon particles to a great extent should not pass through the capillaries of the lungs and deposit in the marrow and the milt.

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[1]) Archiv. f. d. Ges. Physiol. (Pflüger). Bd. 71.

[2]) Berliner Klin. Wochenschr. 1906, N° 28.

[3]) When starving cavies and rabbits usually eat their own faeces, it also often occurs when they have sufficient food.

SWIRSKI: Archiv f. exper. Path. und Pharm. 1902, Bd. 48.

[4]) UFFENHEIMER, after injecting a suspension of prodigiosusbacilli into the rectum of rabbits, noticed a motion of the bacilli in a proximal direction; they ascended up to the pharynx and from thence they were sometimes aspirated into the lungs. Deutsche Med. Wochenschr. 1906, N°. 46.

Description of the Experiments.

1. Cavy 650 grams.

First 24 hours without food, then for 24 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs grey with small black spots, especially in the upper lobes, bronchial glands distinctly pigmented.

Microscop. In the interstitial spaces of the lung-tissue are many cells with black pigment especially under the pleura. A very small quantity of it is also found in the alveolars and in the bronchi. The bronchial glands contain a great many cells with black pigment.

2. Cavy 200 grams.

For 48 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs and bronchial glands pale; microscop. lungs and bronchial glands few cells with black pigment.

3. Cavy 760 grams.

First 24 hours without food, then 5 ccm. of Indian ink in dough, killed after 24 hours.

Results: as in experiment 1.

4. Cavy 350 grams.

First 24 hours without food, then for 48 hours exclusively dough and soot, then killed.

Results: Macroscop. intestines much soot, lungs many black spots and points, bronchial glands pale; microscop. there are foodparticles mixed with soot in many bronchi and alveolars. For a part the soot has already been enclosed in cells, many cells have already penetrated into the interstitial spaces. No pigment is to be seen in the bronchial glands (so in this experiment the coal was aspirated during life; not in agony).

5. Cavy 400 grams.

First 24 hours without food, then 0,5 grams of carmine in dough; killed after 48 hours.

Results: Except in the intestines no carmine can be found.

6. Rabbit 1.75 K.G.

For three days 100 mgr. of soot is brought into the stomach by means of a catheter; killed after 24 hours.

Results: Macroscop. lungs and bronchial glands pale; microscop. few cells with black pigment are to be seen in the interstitial spaces of the pulmonary tissue.

7. Rabbit 2 K.G.

For three days totally 2,9 grams of soot is brought into the stomach with the catheter; killed after 24 hours.

Results: as in experiment 6.

8. Rabbit 2 K.G.

A suspension of 2 grams of carmine in water is brought into the stomach with a catheter; killed after 48 hours.

Results: Except in the intestines, carmine is not to be found.

9. Rabbit 2.75 K.G.

50 grams of charcoalpowder, suspended in water, is brought into the stomach with the catheter; killed after 24 hours.

Results: as in experiment 6.

10. Rabbit 3 K.G.

A suspension of 40 grams of charcoalpowder is brought into the stomach with the catheter; killed after 24 hours.

Results: Macroscop. lungs show black spots especially after dissecting them; the bronchial glands are faintly pigmented; microscop. fine carbon particles and also coarser carbon pieces can be seen in many alveolars. Carbon can be shown neither in the larger bronchi, nor in the trachea; the bronchial glands show some pigment-cells.

The presence of the coarser carbon parts in the alveolars made the diagnose "aspiration" very easy.

11. Rabbit 5 K.G.

After tracheotomy 9 grams of carmine is brought into the stomach with the catheter. About 18 hours afterwards the animal chokes, as phlegm has gathered in the canule.

12. Rabbit 4.25 K.G.

After tracheotomy 8 grams of carmine is brought into the stomach with the catheter; the animal is killed after 24 hours.

13. Rabbit 3.5 K.G.

After tracheotomy 8 grams of carmine is brought into the stomach with the catheter.

Killed after 48 hours.

Results of the experiments 11, 12 and 13: Except in the intestines I could find nowhere carmine in the body at the microscopical investigation; in the lungs and bronchial glands black pigment is present.

14. Cavy 400 grams.

The oesophagus was freeprepared and cut through. Through the lower part 5 gram of vermillion was brought into the stomach. Then the lower part of the oesophagus was bound up whereas the

upper part was fastened with its opening in the wound of the skin.

Killed after 5 hours.

15. Cavy 720 grams.

10 grams of vermillion were injected as in experiment 14.

Killed after 6 hours.

16. Cavy 720 grams.

7 ccm. of a suspension of vermillion in gum arabic was injected as in experiment 14.

Killed after 5 hours.

17. Cavy 400 grams.

2 grams of carmine were injected as in experiment 14.

Killed after 5 hours.

18. Cavy 860 grams.

4 grams of carmine were injected as in experiment 14; killed after 6 hours.

19. Cavy 790 grams.

After laparotomy 4 grams of vermillion (in suspension) were brought into a twist of the intestines; killed after 18 hours.

20. Cavy 620 grams.

6 ccm. suspension of vermillion in gum arabic was brought into the small intestin as in experiment 19; killed after 19 hours.

21. Cavy 750 grams.

10 ccm. suspension of vermillion in gum arabic was brought into the small intestin as in exp. 19; killed with chloroform after 18 hours.

22. Cavy 610 grams.

5 ccm. suspension of vermillion in gum arabic was brought into the colon as in exp. 19; killed after 18 hours, by abruptly decapitating in order to prevent vomiting in agony.

Results of the experiments 14—22: In the lung-tissue and in the bronchial glands no vermillion resp. carmine was to be found.

At experiment 21 the vermillion could also be shown in the stomach, in the oesophagus and in the pharynx while some grains could be shown in the phlegm of the trachea. At experiment 22 vermillion could also be found in the stomach, oesophagus and pharynx whereas in the trachea no vermillion was to be seen. (At the experiment 19 and 20 stomach, pharynx etc. were not investigated).

23. Cavy 700 grams.

After laparotomy 5 ccm. of Indian ink is brought into the small intestines.

Killed after 18 hours.

Results: as in experiment 1.

24. Cavy 880 grams.

After laparotomy 5cm. of Indian ink is brought into the coecum.

Killed after 18 hours.

Results as in experiment 1 (the pigmentation is somewhat less intensive).

25. Cavy 750 grams.

After laparotomy 5ccm. of Indian ink is brought into the small intestines.

Killed after 18 hours.

Results: macroscop. Lungs and bronchial glands pale microscop. few pigmentcells.

26. Cavy 700 grams.

After laparotomy 5ccm. of Indian ink is brought into the coecum.

Killed after 18 hours.

Results as in experiment 1. (here the pigmentation is more intensive.)

27. Cavy 730 grams.

After laparotomy 5ccm. of Indian ink is brought into the small intestine.

Killed after 18 hours.

Results as in experiment 25; one of the mesenteric glands contains carbon parts which are also to be seen microscopically.

28. Cavy 750 grams.

After laparotomy 5 ccm. of Indian ink is brought into the colon at 20 cm. distance of the anus.

Killed after 18 hours.

Results as in experiment 1.

29. Cavy 650 grams.

After laparotomy 4 ccm. of a suspension of ultramarine in 0.9 % NaCl is brought into the small intestines.

Killed with chloroform after 18 hours.

Results: The ultramarine is in the intestines, in the stomach, in the oesophagus and in the pharynx, while some grains can be traced in the phlegm of the trachea, and in that of the chief bronchi.

The pulmonary tissue and the bronchial glands are free of ultramarine.

30. Cavy 850 grams.

After laparotomy 4 ccm. of a suspension of ultramarine in 0.9 % NaCl is brought into the small intestine.

Killed after 17 hours with chloroform.

Results: as in experiment 29; in the phlegm of the trachea and in that of the bronchi however no ultramarine was to be found.

31. Cavy 820 grams.

4 ccm. of ultramarine is administered as in experiment 30.

Killed after $16^1/_2$ hours.

Results: No ultramarine can be found, except in the intestines.

32. Cavy 360 grams.

4 ccm. of ultramarine is brought into the intestines as in experiment 30.

After this the animal is carefully wrapped up so that it can get no faeces into its mouth and cannot lick itself.

After 6 hours the animal is decapitated abruptly in order to prevent vomiting in agony.

Results: the ultramarine is in the small and in the large intestines, also somewhat proximal from the place of injection.

In the stomach, in the oesophagus, in the pharynx and in the phlegm of the chief bronchi no ultramarine can be traced.

33. Cavy 750 grams.

Treated as in experiment 32.

Killed after 16 hours.

Results: as in experiment 32; here some grains of ultramarine are in the stomach.

34. Cavy 475 grams.

Treated as in experiment 32.

Killed after 12 hours.

Results: as in experiment 32.

35. Cavy 540 grams.

Treated as in experiment 32.

Killed after 6 hours.

Results: as in experiment 32.

(March 28, 1907).